

TRANSACTIONS
OF THE
AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS
(INCORPORATED)

Vol. 120

IRON AND STEEL DIVISION
1936

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT THE MEETINGS
HELD AT CHICAGO, OCT. 1-3, 1935 AND AT NEW YORK, FEB. 17-21, 1936

NEW YORK, N. Y.
PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY
29 WEST 39TH STREET

Notice

This volume is the ninth of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928 (later listed as Volume 80 of the TRANSACTIONS)

1929, 1930, 1931, 1932, 1933, 1934, 1935 and 1936, TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the meetings at Chicago, Oct. 1-3, 1935 and New York, Feb. 17-21, 1936.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), Vols. 56 to 72 (1917-1925), and Vols. 73 to 117 (1926-1935), and the indexes in succeeding volumes.

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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

FOREWORD

This presentation in one volume of papers embracing both the fundamental science and the application of fundamentals to the solution of practical problems well illustrates the wide scope and the effectiveness of the Iron and Steel Division's activities.

There is one group of papers on ore preparation and blast-furnace problems, another group on corrosion of steel and high-tensile low-alloy steel, several papers on physical metallurgy, and two on devices for measurement of temperature. Professor Moore's Howe Memorial Lecture on "Correlation Between Metallography and Mechanical Testing" is an outstanding work and should be studied by all metallurgists.

The *Proceedings* of the Division's active Open-hearth Committee, containing papers and discussions on open-hearth problems, are published separately as the "Nineteenth Open-hearth Conference of the A.I.M.E." Likewise, the valuable papers that made up the "Transportation" Symposium, held in conjunction with the Institute of Metals Division, are being published elsewhere. Many of the papers in the present volume have already appeared in *METALS TECHNOLOGY*, and other valuable papers have appeared throughout the year in *MINING AND METALLURGY*.

The effectiveness of the Division's activities and the resultant value to its members are constantly increasing. The addition of a full-time paid Assistant Secretary, Mr. Louis Jordan, much of whose time is being devoted to the work of the Iron and Steel Division, has added much impetus to this movement. Bringing the scientist, the engineer, and the operating man together so that the one can become more conversant with the work and problems of the others is doing much to advance the technology and economy of the iron and steel industry.

CLYDE E. WILLIAMS, *Chairman*,
Iron and Steel Division.

COLUMBUS, OHIO
June 27, 1936

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The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes. By George B. Waterhouse.
- 1934 The Corrosion Problem with Respect to Iron and Steel. By Frank. N. Speller.
- 1935 Problems of Steel Melting. By Earl C. Smith.
- 1936 Correlation between Metallography and Mechanical Testing. By H. F. Moore.



H. F. MOORE

Henry Marion Howe Memorial Lecturer, 1936

Correlation between Metallography and Mechanical Testing

By H. F. MOORE*

(Henry Marion Howe Memorial Lecture †)

SOME sixteen years ago, just after the close of the World War, the opportunity came to me to be in immediate charge of an investigation of the strength of metals under repeated stress—"fatigue of metals" is the popular although rather misleading name. This investigation was sponsored by the National Research Council, and the moving spirit in its organization was the man whose honored name is given to this annual lecture of the American Institute of Mining and Metallurgical Engineers. I can say no words of technical appreciation that will add to the fame of Henry Marion Howe, but would add my tribute of affectionate memory of a man who by his enthusiasm, his help, his criticism, his encouragement helped a young testing engineer in starting and carrying on his first important bit of investigation, and I wish to express my deep appreciation of the honor—and the opportunity—of delivering the 1936 Howe Memorial Lecture.

I am not skilled in the technique of metallography; I am a materials testing engineer who has become keenly aware of the vital importance of metallography to all students and users of the metallic metals of construction. I have come to realize that engineers need an enlarged knowledge of the usefulness, the significance, and the limitations of the metallographic microscope, and of X-rays and gamma rays in the study of metallic materials, and I feel that metallographists may benefit by an enlarged familiarity with the uses and the limitations of testing machines, strain gages, test specimens and other tools of the testing engineer.

Apologies are offered to chemists and students of magnetic analysis for their omission from this correlation picture. Their work is, of course, of very great importance in studying the science of metals, and the only reason for not including it is that such an enlargement of the scope of this lecture would make it altogether too long. The correlation of chemical analysis and the study of magnetic properties with metallography and with mechanical testing is another story—one worth careful telling, some other time.

* Research Professor of Engineering Materials, University of Illinois, Urbana, Ill.

† Presented at the New York Meeting, February, 1936. Thirteenth Annual Lecture. Manuscript received at the office of the Institute Jan. 28, 1936.

A BIT OF HISTORY

About a century after the Pilgrims landed at Plymouth the French Government caused to be made a survey of the manufacturing arts of France, and among the men who made that survey was René Antoine Ferchault de Réaumur (whose name is familiar in connection with the so-called Réaumur thermometer scale). In 1722 he published a monograph entitled "The Transformation of Wrought Iron into Steel." In that monograph he described two rather crude testing machines, one for making tensile tests and the other for making bend tests for ductility.

He also showed a micrograph—hand drawn, of course—showing the structure of steel (Fig. 1). A translation of his remarks on that micrograph seems worth giving here:

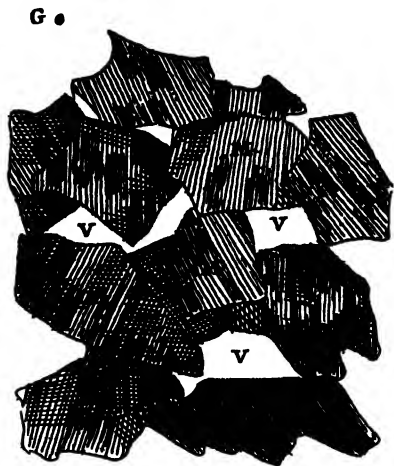


FIG. 1.—GRAIN OF STEEL AS SEEN THROUGH THE MICROSCOPE (RÉAUMUR, 1722).

Let us now consider a grain of steel; a grain which is visible to the unaided eye. That grain, which the eyes perceive easily, is itself an aggregate of other grains which we call "molecules" of that grain. The microscope makes these "molecules" visible to our eyes. *M M M* are the molecules of the grain, the number of which (molecules) is vastly larger than is shown here. The parts that show as white are the voids which are between the different molecules. The molecules of the grain are themselves composed of other parts, which we have called the "elementary" particles of iron and steel.

This is a picture very different from the present-day ideas of the crystalline structure of metals, but it is an interesting pioneer hypothesis.

Now, so far as I can find out, Réaumur suggested no correlation between the structure of steel, as he saw it, and its strength and ductility. That was 214 years ago, and we still find it difficult to correlate the message of the qualitative micrograph and its exhibition of localized irregularities of structure with the quantitative and generalized results of mechanical tests of metals.

TWO GENERAL PROBLEMS OF CORRELATION

In considering correlation between metallography and mechanical testing it seems worth while to consider first, and briefly, two general problems of such correlation: (1) correlation between qualitative and quantitative test results, and (2) correlation between localized and average test results.

Two photomicrographs of steel with the same chemical composition may show markedly different grain structures, as illustrated in Fig. 2. Quantitative measurement of average grain size can be made, and correla-

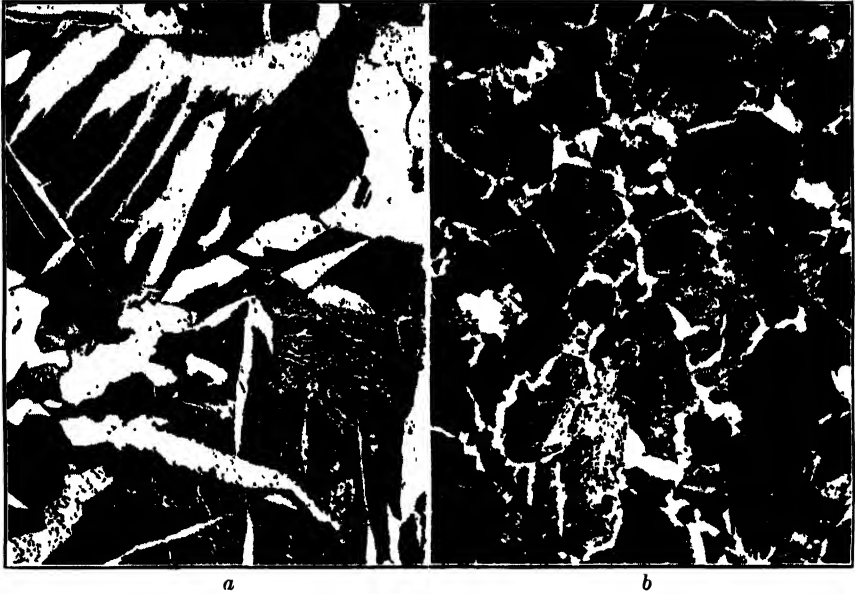


FIG. 2.—DIFFERENT GRAIN STRUCTURE OF TWO PIECES OF STEEL OF SAME CHEMICAL COMPOSITION (0.55 PER CENT CARBON AXLE STEEL). $\times 100$.

a, as forged, *b*, oil-quenched and drawn. Photomicrographs by R. E. Cramer.

tion of that grain size with the quantitative results of a tensile test for strength, but if we try to evaluate the effect of *shape* of grain we find ourselves faced with a different kind of problem. Observations of the

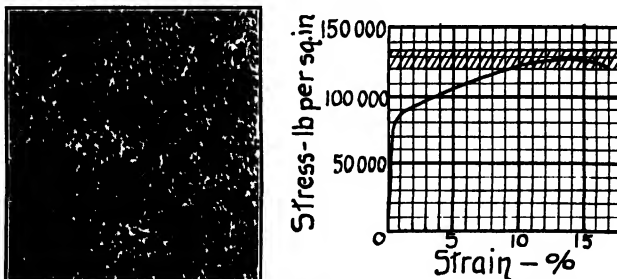


FIG. 3.—PHOTOMICROGRAPH AND TENSILE TEST DIAGRAM (STRESS-STRAIN). HOW CAN WE CORRELATE THEM?

shape of grains are almost entirely qualitative; from such observations we might decide to accept or reject the metal, but we find it difficult to set up formulas or to specify tolerances for such action. The requirement that a specimen of steel shall show a sorbitic structure is a different

kind of requirement from the specification that the tensile strength of the steel shall not be less than 120,000 lb. per sq. in. and not more than 135,000 lb. per sq. in. Fig. 3 may be of aid in visualizing this difference. In the tensile test result the tolerance is clear cut, and, if the test is properly made (note the *if*), the result is almost free from personal opinion. In judging the steel from the micrograph the verdict is "pass" or "fail," and there is a considerable chance for difference of opinion as to whether the structure shown is sorbitic or fine-grained pearlitic.



FIG. 4.—PLASTIC ACTION (SLIP) AND A CRACK IN BOILER PLATE.

Note widespread distribution of "slip lines" and narrow area occupied by crack. Photomicrograph by R. E. Cramer.

The significance of average test results as compared with localized test results may be illustrated by Fig. 4, which shows the structure of a piece of steel that has suffered structural damage by inelastic action (exceeding the yield point) and also by the development of spreading fracture. Structural damage by inelastic action involves a considerable volume of metal. See how widespread are the "slip lines" indicating such action. Except in long compression members, highly localized inelastic action rarely causes appreciable structural damage *so long as nothing but inelastic action takes place*—no spreading cracks, no slow "creep."

On the other hand the *fracture* of a piece of metal, especially under repeated loading, is distinctly a localized phenomenon. In Fig. 4, note how narrow is the area actually cracked. Just how highly localized fracture is in its early stages, we do not know. Is it an atomic phenomenon? A matter of grain strength? Or does it involve several crystalline grains before it really becomes dangerous?

It may be noted that for the problem of elastic failure the results of mechanical tests offer the best quantitative solution, but for the problem of beginning of fracture it looks as if qualitative information from metallographic studies might be the most useful. It seems to me that when the metallographist is dealing with a problem involving the average properties of metallic materials (elastic constants, yield strength, "creep," ductility under static load) he may well look for help from the quantitative results of mechanical tests. When the testing engineer has to deal with a problem involving fracture, he may well be especially alert for qualitative evidence of localized structural damage, evidence which the metallographist can often furnish him.

NEED OF CORRELATION BETWEEN METALLOGRAPHY AND MECHANICAL TESTING

Correlation between metallography and mechanical testing is not going to be an easy task. Is it worth while or will we do well to let these two branches of the science of metals continue to follow separate paths, with few cross paths between them? Up to a short time ago the problem of strength of materials was of interest mainly to civil engineers in connection with structures that had to carry reasonably steady loads. For such structures the development of the mathematical theory of elasticity furnished a satisfactory basis for design, and studies of the crystalline architecture of metals were interesting, but not particularly necessary. The metallographist found his qualitative micrographs of use in connection with the production of metals, and neither metallographists nor engineers paid much attention to the fact that the metallographist had discovered convincing evidence that one, at least, of the fundamental assumptions of the theory of elasticity—namely, the assumption of homogeneity of material—was far from true for the metallic materials of construction. The metals we actually use are evidently *not* homogeneous. They are made up of crystalline grains of various orientation and varying strength, as is illustrated in Fig. 5. They contain nonmetallic inclusions. It is a most interesting technical bit of inconsistency, the fact that metallographists when they have to figure stress or strain use the formulas of a theory that their own discoveries have shown to be founded on an assumption that is not rigidly true for the very metals they study.

It may well be asked why we still continue to apply to actual metals the theory of elasticity if its foundations are not rigidly true. One answer is that, when applied to volumes of metal containing a consider-

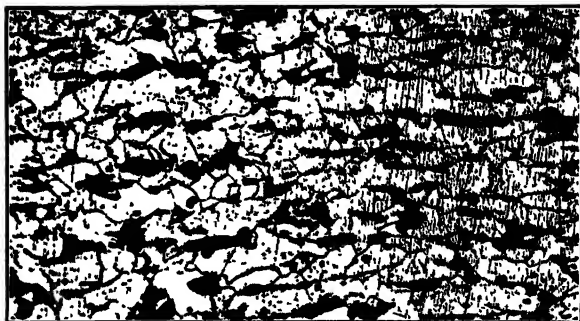


FIG. 5.—PHOTOMICROGRAPH OF STRUCTURAL STEEL CAN THIS METAL BE REGARDED AS HOMOGENEOUS?

able number of crystalline grains, the assumption of homogeneity is “statistically” accurate. This is illustrated, or rather cartooned, in Fig. 6. The behavior of a volume of metal containing, say, a thousand crystalline grains can be predicted by the theory of elasticity, just as the rate of mortality for a large group can be predicted by an insurance

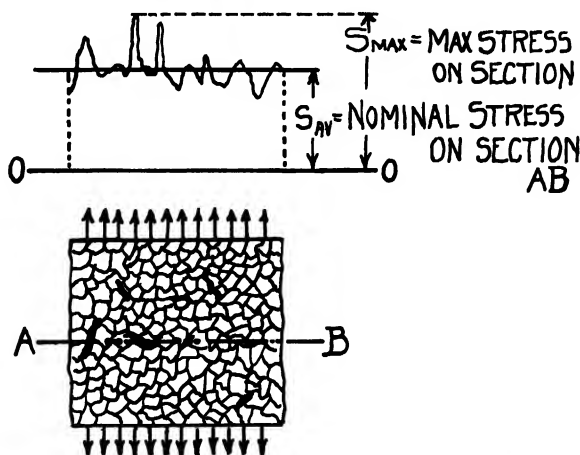


FIG. 6 —NOMINAL AND ACTUAL STRESS UNDER TENSION.

This figure is to be regarded as a cartoon of stress distribution rather than as a diagram based on accurate measurements.

actuary. When we come to minute areas, such as the area at the root of a screw thread, the limitations of the theory of elasticity begin to become noticeable. Even in that connection the theory is useful to the engineer, because, in all cases so far studied, it predicts stresses and strains higher than those that actually are present; it gives results on

the safe side. Another reason why it is still used, and will in all probability be used for a long time yet, is that no other usable theory has as yet been developed.

Obviously, as the limitations of our common theory of strength of materials become more and more significant, and the knowledge of the actual structure of metals becomes broader, there will be a growing need for the metallographist and the engineer to work together to devise correction factors for the theory of elasticity when minute stress areas in machine parts are under consideration. Perhaps some day we may devise a more nearly perfect theory of the strength of materials, but no such development is in sight at the present time.

In connection with the use of the common formulas for strength of materials, I cannot resist the temptation to throw a stone at my pet aversion—formula worship. A nice smooth stone is furnished by some psalmlike verses by Dean R. D. Carmichael, of the University of Illinois Graduate School, verses that appeared in the *Scientific Monthly* for December, 1935 (p. 496):

He that seeketh to *compute* his way to the wonders of mathematics
 And delighteth not in ideas
 Shall be grievously tormented:
 In anguish shall he die in the wild jungle of formulas,
 His heart shall be pierced by the poisonous symbols:
 But he that meditateth frequently in silence
 And seeth the truth oft without symbols
 And delighteth much in ideas comprehended
 Shall get marvelous strength from the dangerous symbols
 And tame the jungles of wild formulas;
 He shall roam at his will in their borders,
 Constraining their giants to do his bidding,
 Unfolding the truth for the ages;
 And in joy he shall bring the gift of his thinking
 And bestow upon man a perpetual blessing,
 And for a while he shall be gratefully remembered:
 But he that seeketh to compute his way to the goods of the science
 And delighteth not in ideas
 Shall be grievously tormented,
 In anguish shall he die in the jungles of wild formulas,
 And oblivion shall cover him over with kindly forgetfulness.

And to these verses may we add a commandment against formula-dolatry:

Before thou usest a formula thou shalt examine thyself and see to it that thou knowest what each symbol therein meaneth, and in what units it is measured; moreover thou shalt consider the limitations of thy formula and shalt not transgress them.

CORRELATION ALREADY ACCOMPLISHED

In order to take a cheerful view of our subject, may we now consider some of the fields in which effective correlation between metallography

and mechanical testing have been achieved. Perhaps the most obvious example of such achievement is found in the development of the heat-treatment of metals. Within the lifetime of most of those present, this has been changed from a rule-of-thumb art to a fairly definite science. And throughout this development the microscope, the pyrometer and the testing machine have been active partners. The microscope has thrown light on the mechanism of the changes in structure due to heat-treating

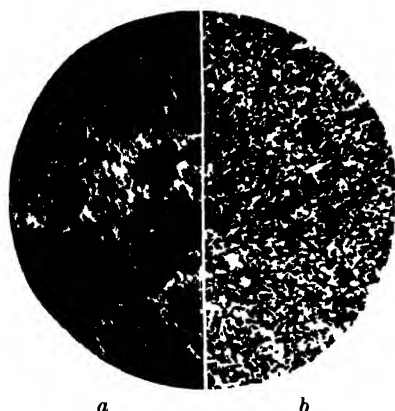


FIG 7.—CHANGE IN CRYSTALLINE STRUCTURE DUE TO HEAT-TREATMENT; 0.37 PER CENT CARBON STEEL. $\times 100$.

a, normalized at 843°C ., b, water-quenched from 843°C ., drawn at 566°C . Photomicrographs by J. W. Harsch.

(this is illustrated by Fig. 7), the pyrometer has changed heat control from skilled guesswork to a quantitative process with narrow tolerances, the testing machine has given a quantitative measure of the effects achieved—by no means a perfect measure, but one far more valuable for predicting serviceability than the qualitative opinions of the old days of heat-treating. Then too this cooperation has very greatly widened the field of heat-treating. It has made common the use of heat-treating to gain strength as well as cutting hardness. In my days in the college shop course I learned that only the higher carbon steels could be affected

by heat-treatment, although I believe there was a growing belief that nickel might be used in place of some of the carbon. I have myself lived long enough to harden and strengthen Armco iron by heat-treatment—not very much, but appreciably. Now we are beginning to realize the possibilities of heat-treatment in the nonferrous field. I believe that the progress in this field would have been much slower had there not been a good degree of correlation between metallography and mechanical testing.

Another field of study in which correlation between metallography and mechanical testing has been fruitful includes the study of the elastic strength of metals. Before the days of the metallurgical microscope the “elastic limit” of a metal was supposed to be a definite stress value marking a sharp dividing line between pure elastic action and the beginning of plastic action. It was commonly assumed, although without any good grounds for the assumption, that so long as a metal obeyed Hooke’s law its action was elastic, and, conversely, so long as its action was elastic it obeyed Hooke’s law (see Fig. 8, a and b). There grew up a belief in what Prof. Frederick Bacon, of Swansea, Wales, has called “that mythical idol the ‘true’ elastic limit.”

The metallographic work of Ewing, Rosenhain and Humfrey¹ threw a bright light on the mechanism of plastic action. Fig. 9 is a dark-field photomicrograph of iron in which a few crystalline grains have begun to show "slip lines"; the commonest metallographic sign of plastic action. It is doubtful whether even with our most delicate strainometers we could detect inelastic action as small as this. Then when we try to determine "true" elastic limit (or proportional limit, for that matter) we find that the value determined is a function of delicacy of apparatus.

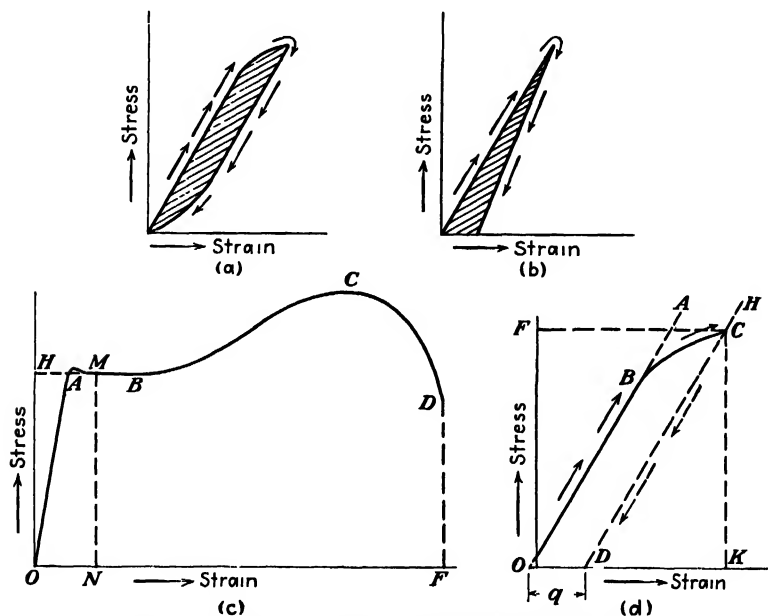


FIG. 8.—VARIOUS TYPES OF STRESS-STRAIN DIAGRAM

- a. Proportional limit exceeded without permanent set The stress-strain diagram of rubber under low stress approximates this type
 b Set developed without exceeding proportional limit Very few, if any, actual structural materials show this type.
 c Metal with well marked yield point.
 d. Metal with no well marked yield point.

Fig. 10 shows some results obtained from various laboratories, and plotted by J. B. Romer, of the Babcock and Wilcox laboratories.

The correlation of metallographic study and mechanical testing have changed (and I believe have made more accurate) our ideas about elastic strength. The important index of elastic strength is the limiting stress below which inelastic action is *not sufficient to cause structural damage*. What constitutes "structural damage" will be different for different metals and for different uses of the same metal. For example, the allowable amount of inelastic action in the tension members of a bridge

¹ *Phil. Trans. Royal Soc.* (1899) **193**, 352, and (1903) **200**, 241.

truss is much greater than that allowable in the metal of the tube of a Bourdon pressure gage. The determination of safe tolerances of inelastic



FIG. 9.—EARLY STAGE OF PLASTIC ACTION IN ARMCO IRON

Note beginning of slip as shown by slip lines in a few crystalline grains (*S, S*). It is doubtful whether this degree of plastic action could be detected by an extensometer of the sensitivity commonly used in careful laboratory tests.

action is a matter for the users of any given metal to specify. For many structural metals 0.2 per cent inelastic strain seems to be a fairly satis-

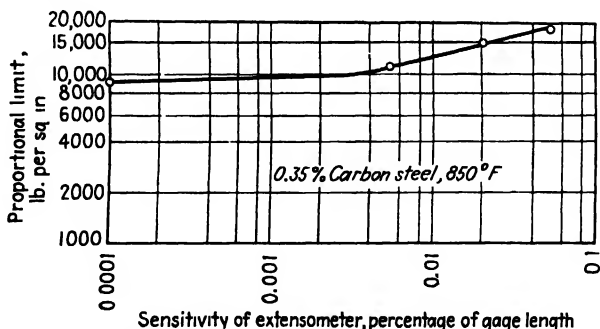


FIG. 10.—DEPENDENCE OF PROPORTIONAL LIMIT ON SENSITIVITY OF STRAIN MEASUREMENT.

factory limit, although to me it seems rather high². The percentage of permanent set remaining after release of load is the most obvious index of inelastic action, and this set can be measured with a good degree of

² For a discussion of methods of determining elastic strength and for a short list of allowable values of inelastic action specified for metals, see the 1935 Tentative Standards of the American Society for Testing Materials, pp. 1440–1443, inclusive.

accuracy by measuring the deviation of the stress-strain diagram from a straight line. Figs. 8c and 8d illustrate the determination of a practical elastic strength from the stress-strain diagram, and the name "yield strength" has been tentatively given to this index of elastic strength. In using this, or any other, index of elastic strength the limiting tolerance of inelastic action should be stated. Thus yield strength ($q = 0.1$ per cent) = 36,700 lb. per sq. in. (q as shown in Fig. 8d). In many papers, especially from foreign laboratories, values of "elastic limit" are frequently reported, with no statement of the tolerance of inelastic action used—if, indeed, any definite tolerance was used. Such values have comparatively little significance, although I will admit that in my earlier testing days I frequently reported such values.

I note that I have been indulging myself in a short canter on one of my hobbies, and would bring attention to the fact that correlation of metallographic study and mechanical testing has been fruitful in clarifying our ideas about elastic strength of metals; the development of the Jeffries-Archer slip-interference theory³ is an illustration. This theory pictures inelastic action as starting as slip within a crystalline grain of metal, spreading to the grain boundary, and possibly finding its progress somewhat hindered there. After crossing the boundary, slip may be still further hindered by grains that are stronger either by virtue of their atomic orientation or their composition. There is an optimum size for resisting power of grains to slip—different for different metals, of course. This picture and Romer's picture of "elastic limit" as a function of sensitivity of apparatus fit together nicely, and seem to be a more useful concept than the old idea of the "true" elastic limit.

SOME FIELDS IN WHICH CORRELATION IS TAKING PLACE

As noted previously, quantitative study of effect of grain size is taking place in metallographic laboratories. I can only refer to the recent remarkable developments of the McQuaid-Ehn test, with its emphasis both on the qualitative "normality" or "abnormality" of steel and on the quantitative factor of inherent grain size⁴.

This matter of grain size, and of size of specimen, has recently appeared in connection with the sensitivity of different metals to notches and other "stress raisers." If we make fatigue tests on two sets of *small* specimens of fine-grained metal—one set notched and the other unnotched—the specimens with notches develop a fatigue limit much below that of the unnotched specimens. If then we make fatigue tests on two corre-

³ For a statement of this theory see *Chem. & Met. Eng.* (June 15, 1921) 1057; also the book, *The Science of Metals*, by Jeffries and Archer.

⁴ H. W. McQuaid and E. W. Ehn: Effect of Quality of Steel on Case-carburizing Results *Trans A I M E* (1922) 67; also *National Metals Handbook* (1933) 644-649, inclusive.

sponding sets of small specimens of coarse-grained metal, the weakening effect of the notch is usually much smaller than for the fine-grained metal. However, R. E. Peterson, of the Westinghouse laboratories, has recently reported that if corresponding fatigue tests are made on *large* specimens both fine-grained metal and coarse-grained metal show a percentage weakening due to notch about as large as the percentage weakening for the small specimens of fine-grained material. Peterson made the

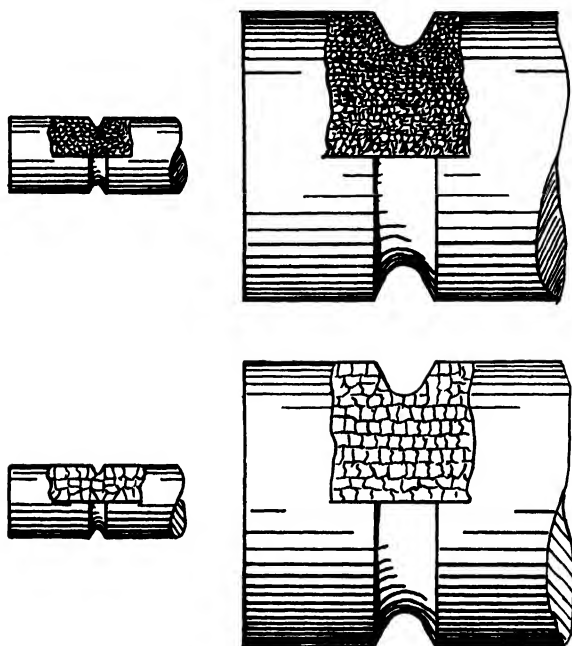


FIG. 11.—NOTCH EFFECT, LARGE AND SMALL SPECIMENS; FINE-GRAINED AND COARSE-GRAINED METAL.

dimensions of the notches in his large specimens geometrically similar to the dimensions of the notches in the small specimens.

Fig. 11 illustrates, or rather cartoons, the conditions of the tests. I would suggest the following hypothesis for Peterson's results. A fatigue crack starts in the same direction as that of plastic action (slip). That direction is always in one of the planes of maximum atomic weakness, even if that plane of weakness is not a plane perpendicular to a maximum tensile stress. In a member subjected to tension or to flexure this crack follows this plane of atomic weakness until it reaches a crystalline grain boundary, then changes direction as it crosses the boundary into another grain with different orientation of its planes of weakness. As the crack crosses grain boundaries there seems to be a tendency for it to take up a direction perpendicular to the principal tensile stress; and the

final fracture looks, to the unaided eye, as if it were a crack perpendicular to the principal tensile stress.

The particular plane of weakness along which a crack starts is that plane of weakness on which the component of the nominal shearing stress is a maximum^b. Now in flexural specimens such as those shown in Fig. 11 the principal tensile stress is in a longitudinal direction, and at the surface the maximum shearing stress is in the direction of 45° with the

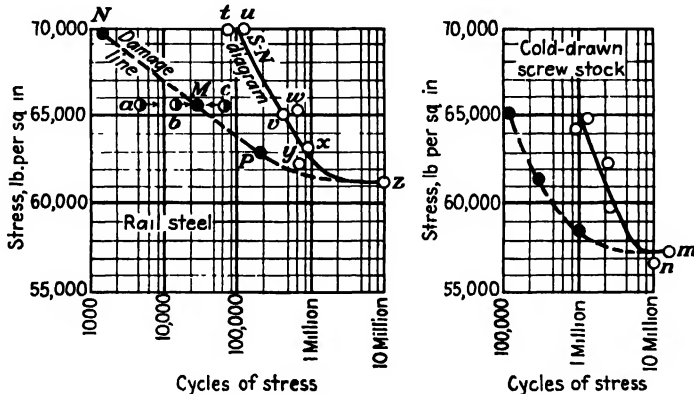


FIG. 12.—“DAMAGE LINE” DIAGRAMS.

These “damage lines” indicate limits of stress and number of cycles that cause structural damage to a metal, as shown by reduction of its virgin endurance limit.

principal tensile stress. In a small specimen of a large-grained metal the crack would tend to *start* in a diagonal direction (on the plane of atomic weakness most nearly in the direction of maximum shearing stress). It tends to spread beyond the region of high nominal stress near the root of the notch before it crosses many grain boundaries and would not get a chance to start in a circumferential direction perpendicular to the principal tensile stress, as cracks usually do after they have spread a small distance. In all the fine-grained metal specimens, and the *large* specimens of coarse-grained metal, a crack once started would traverse several grain boundaries before it got beyond the region of high stress near the root of the notch and would have a good chance to start on its destructive spread in a circumferential direction.

The question, “When does a fatigue crack start, anyhow?” is still waiting a fully satisfactory answer, and I am glad to note that the question is being attacked by means of the testing machine, the metalurgical microscope, and a study of X-ray diffraction. H. J. French, of the International Nickel Company’s laboratories, has done pioneer work in determining what he calls the “probable damage line” as an important

^b H. J. Gough: Crystalline Structure in Relation to Failure of Metals—Especially by Fatigue. *Proc Amer Soc Test Mats.* (1933) **33**, pt. II, 3–114, especially 21–39, inclusive. This paper was the 1933 Marburg lecture, and is in itself an excellent example of correlation of metallography with mechanical testing.

part of the fatigue-test diagram. Fig. 12 shows two "damage-line" diagrams. For any given metal the endurance limit is determined in the usual way; then, for any given stress above this endurance limit the approximate number of cycles of this overstress that can be applied to the metal without reducing its virgin endurance limit is determined as shown in Fig. 12. Determining this number of cycles for several stresses, several points on the "probable damage line" are located and the line drawn. In the region to the left of the damage line it is judged that no



FIG. 13.—FATIGUE CRACK IN MONEL METAL. ORIGINAL MAGNIFICATION 1300. REDUCED ONE-FOURTH IN REPRODUCTION.

The crack seems to have started near the middle of the area shown and to have spread both ways. For some distance it seems to extend parallel to slip lines, then to tend to depart from that direction, presumably turning toward a direction at right angles to the direction of the principal tensile stress. Photomicrograph by Prof. Tibor Ver, of Budapest.

serious fatigue damage has been suffered by the metal, since its virgin endurance limit has not been lowered by overstress; in the region between the damage line and the stress-cycle ($S-N$) diagram fatigue damage has been done. A number of laboratories are following up this method of study, which, it is hoped, may be used to determine combinations of stress and cycles that may be expected to start destructive fatigue cracks.

At the Massachusetts Institute of Technology, Prof. A. V. de Forest is using direct examination through the microscope to study fatigue cracks in the early stages of their developments. Fig. 13, a photomicrograph by Professor Ver, of Budapest, obtained in the metallographic laboratory of the University of Illinois, shows a fatigue crack in a copper-nickel alloy. The crack seems to have started parallel to

slip lines and to have changed its direction as it spread, presumably to a direction perpendicular to the principal tensile stress.

A very interesting correlation is now being worked out by two committees of the American Society for Testing Materials, the Research Committee on Fatigue of Metals and the Committee on Metallography. Those committees are making an attempt to find some correlation between the indications of X-ray diffraction apparatus and the behavior

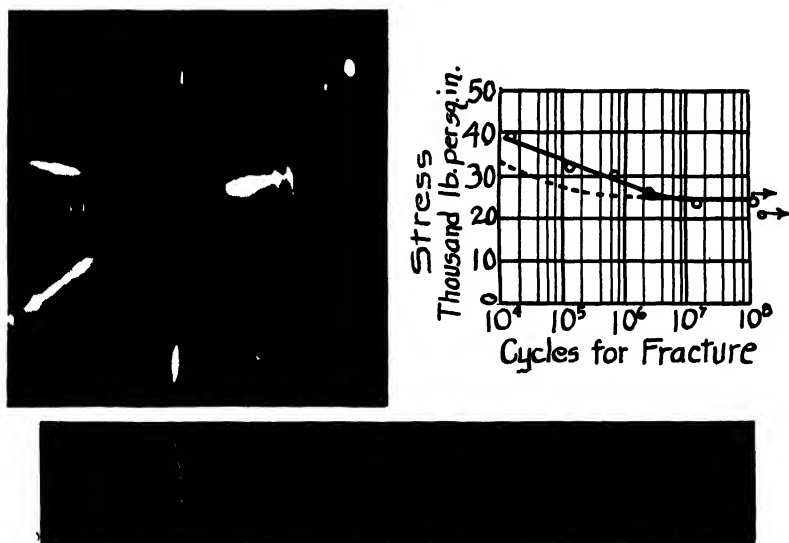


FIG. 14.—X-RAY DIFFRACTION PATTERNS AND STRESS-CYCLE (*S-N*) DIAGRAM OF FATIGUE TEST. CAN THESE BE CORRELATED?

of metals in repeated-stress testing machines. Fig. 14 pictures typical results of the two kinds of tests. X-ray diffraction sometimes shows a type of pattern that is said to indicate "fragmentation" (Fig. 15). Whether this "fragmentation" is an indication of structural damage—destructive cracking—or indicates a slight noninjurious disturbance in the regularity in the orientation of the squads of regularly arranged atoms—the space lattice units—is uncertain.

The correlation of X-ray diffraction and strength and ductility values is of especially great difficulty. The X-ray experimenter brings to the engineer a series of, say, Laue diagrams and calls this one "good" and another one "bad." The engineer can see differences in the diagrams, but cannot see how that difference can be expressed in any quantitative way. The X-ray experimenter then speaks of differences in width of lines or of shift of lines which can be measured quantitatively, but so far he speaks hopefully rather than assuredly. Then, too, these X-ray diffraction indications are, in general, indications of general atomic arrangement within a crystalline grain. Any defects they indicate are

systematic defects rather than localized defects. The engineer, especially the mechanical engineer, is very much interested in *localized* defects, defects that indicate danger of fracture, which is emphatically a localized phenomenon. Again we may use the life insurance analogy. The X-ray investigator may be compared to the actuary who can predict the

general scheme of distribution of mortality in the city of New York during 1936, while the engineer may be compared to the man who asks whether there will be a death in his family during the same period. At present the X-ray experimenter cannot answer the engineer's questions. However, two facts must be kept in mind: (1) the development of X-ray diffraction analysis is in its early stages, and (2) it is the only experimental tool we have for studying the structural architecture of metals in fields too small for the microscope. Correlation is difficult, but its possibilities of value are so great that the search for connection between X-ray diffraction and mechanical test results is a most attractive research adventure.

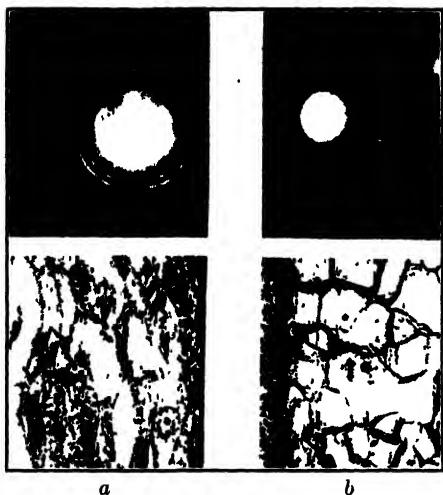


FIG. 15 —X-RAY DIFFRACTION PATTERNS (ABOVE) AND PHOTOMICROGRAPHS (BELOW) OF COLD-DRAWN STEEL AND ANNEALED COLD-DRAWN STEEL

a Cold-drawn steel. Diffraction pattern indicates "fragmentation." Does "fragmentation" indicate incipient structural damage, or merely a noninjurious disturbance of atomic arrangement?

b. Same steel annealed

SOME UNSOLVED PROBLEMS WHICH REQUIRE CORRELATION

May we now consider a few of the many unsolved problems of metallic materials, problems that will require for their solution correlation of metallographic and mechanical methods. The elasticians have developed an elaborate system of computation of stresses and strains, and where their methods lead to differential equations beyond the methods of solution now available—and frequently they do lead to such equations—it is often possible to use mechanical, optical or electrical devices for the practical solution of these equations; such, for example, as the examination of stressed specimens of transparent material by means of polarized light. But the mathematical theory of elasticity, even with such aids, cannot tell us what magnitudes of stress, strain or strain energy cause *structural damage* to different metals under various conditions of localization of stress, of rapidity and repetition of loading, or of combinations of stress in different directions. Engineers and

elasticians have worked out at least five theories of failure of materials. These theories are shown diagrammatically in Fig. 16. They are all based on ideal elastic materials, homogeneous and isotropic. It is not strange that, applied to actual metals, actual test results show a "scatter" so wide as to make it difficult to distinguish between the relative validity of the different theories⁶. In solving this problem engineers have not

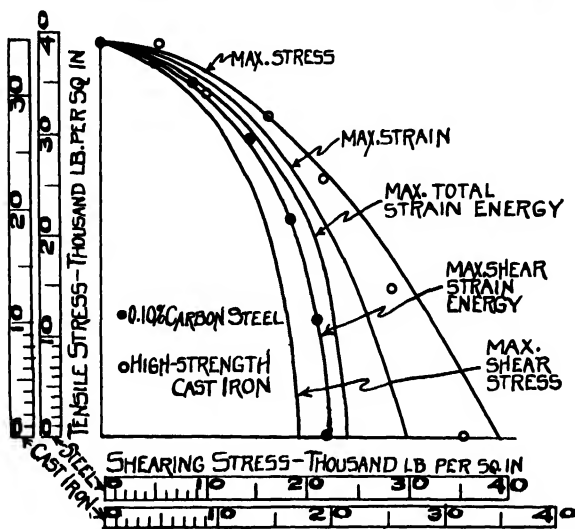


FIG. 16 — DIAGRAMS FOR VARIOUS THEORIES OF FAILURE

Ordinate and abscissa of any point on any curve shows a combination of shearing stress and tensile stress supposed to cause failure. Test results plotted for steel and for cast iron are results of fatigue tests reported by Gough at the National Physical Laboratory, England.

cooperated effectively with metallographists, but they should do so. Already metallographists have drawn qualitative pictures, or at best semi-quantitative pictures of the mechanism of failure. These are cartooned in Fig. 17. Griffith⁷, with the concept of submicroscopic cracks as the source of failure, Joffé⁸ with the theory of surface imperfections as the starting point of failure, Zwicky⁹ with his theory of planes

⁶ The theory I have found most satisfactory for ductile metals is the Von Mises-Hencky theory that it is energy of shearing strain that causes failure, although the simpler theory that maximum shearing stress is the cause serves very well. For brittle metals the evidence is much less complete, but it seems to indicate that failure results either from maximum tensile (or compressive) stress, or from maximum strain. Test results fall in between results computed by the two theories

⁷ A. A. Griffith: Phenomena of Flow and Rupture in Solids. *Phil. Trans Royal Soc* (1920) A-221, 163.

⁸ A. F. Joffé: The Physics of Crystals. New York, 1928. McGraw-Hill Book Co.

⁹ F. Zwicky: On the Imperfections of Crystals *Proc Nat Acad Sci* (March, 1929) 15, No 3, 253

On Mosaic Crystals. *Idem.* (Nov., 1929) 15, No. 11, 816.

of weakness due to a combination of space lattice dimensions together with differently spaced planes of weakness due to thermal atomic vibra-

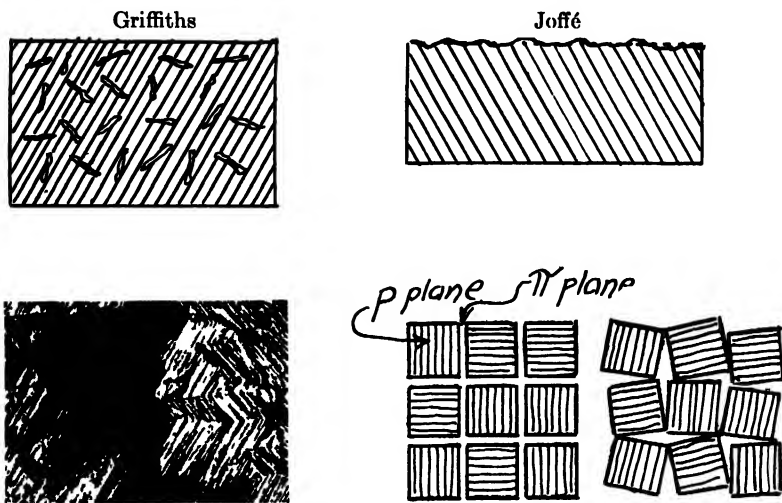


FIG. 17—CARTOON DIAGRAMS ILLUSTRATING VARIOUS THEORIES OF MECHANISM OF FAILURE CAN THESE THEORIES AND THOSE ILLUSTRATED IN FIG. 16 BE CORRELATED?

tions, Davey¹⁰ with his theory of regularly spaced planes of weakness naturally occurring in grains and between grains during the process of solidification—all these men have given us pictures of states of affairs that show how much more complicated is the actual strength of a material than is the resistance of atoms to being pulled apart. It seems difficult to plan any correlation between these pictures and the engineer's quantitative theories of failure. Yet the search for a theory or theories which shall be consistent with at least one of the metallographist's pictures and with the engineer's need for a quantitative theory—that search seems well worth while.

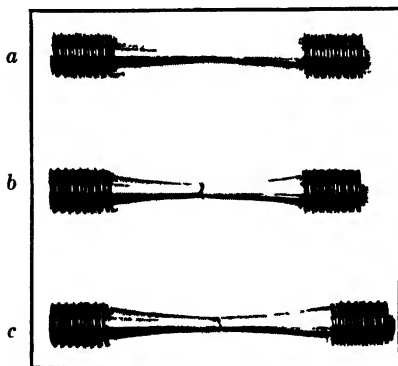


FIG. 18—TENSILE FRACTURES OF "DUCTILE" METAL

- a Unstressed specimen.
- b Specimen after fracture under tens of thousands of cycles of repeated tensile stress (no reversal of stress).
- c Specimen after fracture in ordinary tension test.

Another unsolved problem concerns itself with the nature, the significance, and tests for ductility and brittleness. The conventional answer to the question "What is duc-

¹⁰ W. P. Davey: The Mechanism of Crystal Growth *Trans. Amer. Soc. Steel Treat.* (Nov., 1933) **21**, No. 11, 965.

tility?" would define it as the quality shown by great elongation and reduction of area in a tensile test. But that answer is not very satisfactory. Some metals that, judged by this criterion, show high ductility, develop cracks after a relatively few cycles of repeated stress, especially repeated stress at notches (Fig. 18). A good elongation and reduction of area does not guarantee satisfactory freedom from cracking under thousands or millions of stresses which cause slight localized plastic action. In this connection we must face the fact that under service conditions there is slight plastic action at dozens of minute areas in most machine parts, and in some structural members. Fig. 19 shows some typical cases of "stress raisers," which cause local stress concentration. As a matter of fact, if it were not for

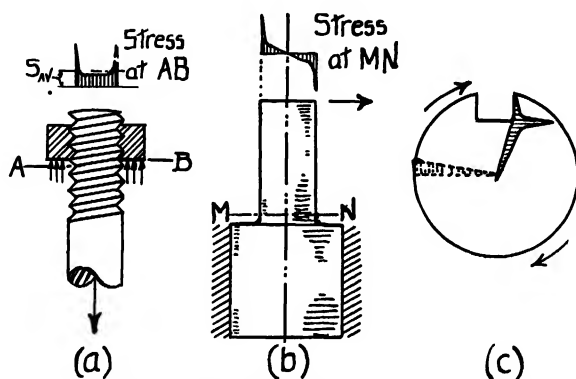


FIG. 19 — TYPICAL "STRESS RAISERS" IN MACHINE AND STRUCTURAL PARTS

this slight plastic action few, if any, of our machine parts would hold together. The beneficial effect of slight, crackless plastic action in easing overstress, and thus preventing spreading cracks, is probably the salvation of many a crank pin and railroad rail. Professor Seely, at Illinois, recently uttered a striking epigram: "The reason why we can use the theory of elasticity for designing actual structures and machines is that our actual materials are not perfectly elastic."

Now this study of ductility and brittleness will call for cooperation between metallographists and testing engineers. What are the metallographic signs of incipient structural damage? Many gazers through microscopes have reported that damage in a metal usually starts *within* a crystalline grain, but the detection of its very beginning is a task to strain the powers of the microscope to the utmost. However, microscopic examination has shown what seem to be planes of weakness within the crystalline grain, and the test results from X-ray diffraction apparatus indicates that there should be such planes, while the work of the testing engineer has shown that the planes on which failure begins seem to coincide with the planes that have aroused the suspicions of the X-ray

worker. Most of these results come from tests of single crystals of metals. How does structural damage spread from one grain to another? What happens when a spreading crack runs into a stronger grain? Can we develop a crack-interference theory analogous to the Jeffries-Archer slip-interference theory? When we apply metallographic methods to this study of the origin of structural damage we are faced with the fact that it is not at all certain in which one of several hundred (or thousand) grains that damage will start. The poor metallographist must start a search for a very small needle in a very large haystack. However, we

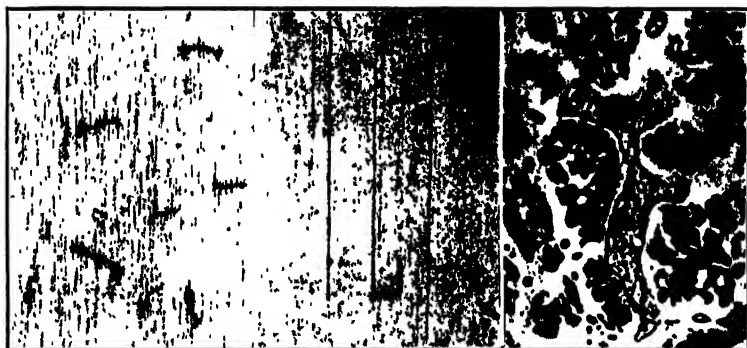
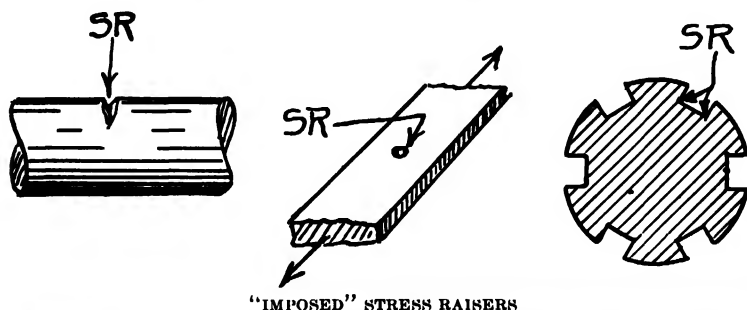


FIG 20—"INHERENT" AND "IMPOSED" STRESS RAISERS

engineers have faith enough in you metallographists to believe that you will find some means of investigating structural units of metals, units smaller than the crystalline grain and larger than the well ordered squad of atoms that makes up the space lattice unit. Then between us we shall have to fit some quantitative formulas to the findings.

Yet another field in which correlation of metallographic and mechanical methods is needed is the study of the relative seriousness of "inherent" and "imposed" sources of stress concentration—"stress raisers," as Gillett has aptly called them. I use the term "inherent" to denote stress raisers existing in the structure of a metal—shatter cracks, non-metallic inclusions, dendritic crystals, slag streaks and the like. Typical

"inherent" stress raisers are shown in the lower part of Fig. 20. I use the term "imposed" to denote stress raisers caused by sudden changes in form—such things as screw threads, notches, sharp shoulders and the like, some of which are shown in the upper part of Fig. 20. So far the meager data indicate that stress raisers that are outright discontinuities in structure, such as shatter cracks in railroad rails or sharp notches in machine parts, seem to be much more serious than stress raisers that do not cause discontinuity of structure—such as slag streaks, large or irregular crystals, etc.¹¹ Then there is the disconcerting result of some tests which seem to show that even discontinuities like scatter cracks do not cause as much weakening of structure as would appear from the formulas of the theory of elasticity. The good-natured ductility of metal around these discontinuities does its best to ease off the localized stress and distribute it over a larger area, but there is a limit to this good-natured ductility and then spreading fracture starts.

Surely further study of the relative seriousness of various types of metallographic imperfections of structure and of mechanical imperfections of form afford a fertile field for joint study by metallographists and testing engineers.

THE "FRAME OF MIND" FOR CORRELATION

Perhaps after all the greatest problem in bringing about correlation between metallography and mechanical testing is the building up an intelligent interest in the other fellow's field of work. May I illustrate by an experience. A young student of metallography brought a specimen of an alloy to the materials testing laboratory. He had poured the molten metal into a metal mold, had taken the solidified piece to the machine shop for machining into shape as a tensile test specimen. The machine work was very poor, with deep tool marks on the surface of the specimen. He was a careful student in chemistry and in metallography, yet he proposed to draw conclusions as to the mechanical properties of the alloy from test results on one defective specimen of cast metal. This, of course, was an extreme case, and similar stories could be told by chemists and metallographists about engineers.

The testing engineer and the metallographist need to learn something of the necessary refinements and the limitations of test results in the other fellow's field. The engineer does not realize the difficulty of picking out the part of the specimen that shows a characteristic structure, or that shows some special metallographic feature; he does not appreciate difference in results which can be caused by variation of etching, lighting and photographic technique. The metallographist does not always

¹¹ Graphite flakes in cast iron act like discontinuities. Gray cast iron may be regarded as iron containing many cracks filled with a lubricant.

realize the possibilities of serious error in mechanical test results due to improper gripping of specimens (especially specimens of brittle metal, Fig. 21), to the use of too high a speed in testing, to the use of too large a testing machine for small specimens, to improper attachment of strain-measuring apparatus. Discriminating appreciation of the other fellow's field of work is a prime requisite for effective correlation of test results.

There should be more correlation between metallography and mechanical testing during student days. There could be curricula in which the metallographist will acquire considerable skill in the technique of the metallurgical microscope, and possibly in the use of the X-ray

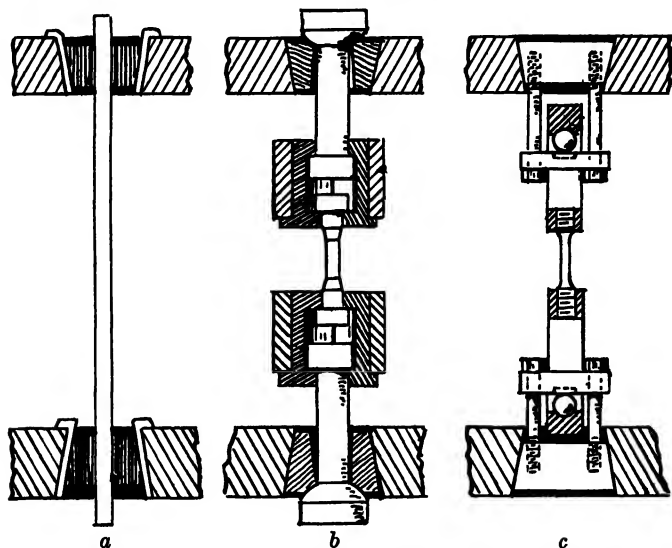


FIG. 21.—GRIPS FOR TENSION TESTS.

- a. Wedge grips suitable only for tension tests of long pieces of ductile metal.
- b. Spherical seated grips suitable for tension tests of long or short specimens of high or moderate ductility.
- c. "Robertson shackles" (ball bearing on flat plate), desirable for tension tests of brittle metals.

diffraction apparatus, while at the same time he is given what might be called a "course in appreciation" in mechanical testing, in which he would not spend the time necessary to acquire skill in technique, but would learn the major difficulties in carrying out accurate, reliable and significant mechanical tests. An analogous course might be carried out for the engineer. The suggestion of any addition to our already overcrowded curricula is always a hazardous one to make, but at least "appreciation courses" in mechanical testing and in metallography could be placed on the short list of electives offered in connection with most engineering and metallurgical curricula. Appreciation courses have worked well in the field of music; are they not worth trying in the technical field?

The jack of all trades and master of none is not an honored character, and I have no desire to see any student of materials of construction become a "jack" in both metallography and mechanical testing. However, the jack of *several* trades and master of *one* is a very useful person, and has in his familiarity with and appreciation of several trades a pretty effective safeguard against narrow-minded specialization.

When testing engineers come to recognize the importance, the significance and the limitations of micrographs and of X-ray diffraction patterns, and when metallographists come to recognize the importance, the significance, and the limitations of accurate technique in mechanical testing, and of stress-strain diagrams and stress-cycle diagrams and impact-test results, then we shall have gone a long way on the journey of correlation between metallography and mechanical testing, the journey which Réaumur started 'way back in 1722.

Five Years of Progress in Southern Blast-furnace Practice

By FRANCIS H. CROCKARD, * ASSOCIATE MEMBER, A.I.M.E.

(Chicago Meeting, October, 1935)

DURING the past five years we have probably witnessed greater technological advances than in any similar period. Industry and science have steadily marched ahead. The makers of iron and steel products have watched with great interest the development of streamlined trains, faster and safer airplanes, the entirely new science of air-conditioning and the widespread use of stainless steels. Since 1930, we have witnessed the erection of the world's largest suspension bridge, the largest and fastest ocean liner and the spectacular Boulder Dam, while even greater things are planned in these particular fields. Other industries, too, have been moving ahead rapidly.

This advance in a few years has been caused primarily by the fierce competition of the depression. Now, more than ever, is the emphasis placed upon quality and service. Makers of southern merchant pig iron have been no exception and have been confronted with increasingly strict chemical specifications and with much greater stress on physical characteristics than ever before.

For example, sulfur in the iron must be held very low, competition demanding that it be in the 0.020's and low 0.030's; silicon content must be held within a very narrow range, and definite requirements of phosphorus and manganese are an essential part of the specifications.

Physical characteristics are becoming of increasingly greater importance. The introduction of triple-skimmed, slow-cooled iron several years ago was the first step in this direction. Now there are a few customers who buy iron by chemical analysis *and* physical appearance, having found that the analysis alone is an insufficient guide to their requirements.

In addition to questions of quality, the subject of cost has greatly altered the southern furnaceman's viewpoint on many things. Formerly we had low-grade but cheap raw materials, but recent developments, such as greatly increased labor rates, have raised the cost of the same

Manuscript received at the office of the Institute Aug. 15, 1935.

* Metallurgist, Republic Steel Corporation, Southern District, Birmingham, Alabama. Recipient of J. E. Johnson, Jr., Award, 1936.

quality of ores. This has resulted in the increased use of labor-saving devices and a much closer watch over the economical use of raw materials. A survey of the more important trends of the past few years, therefore, should be of interest.

COKE QUALITY

It is, of course, easier to dispose of a low-grade product by using it yourself than by selling it. The converse has also been true; namely, if it is for your own use it need not measure up to commercial standards. The fallacy of this is that by using lower grades you are actually putting yourself at a disadvantage. To make a final product of high quality, raw materials of high quality are essential.

A case in point is in the manufacture of blast-furnace coke. Most furnaces are operated in conjunction with a coke plant, but the coke-plant operators frequently are forced to keep their eyes on the market for commercial coke, byproducts, etc., and to operate the ovens accordingly, with the result that the furnace coke sometimes suffers. Recently we have focused a great deal of attention on the improvement of furnace coke, and the results have been felt in improved practice at the furnace. Most southern coals that are coked for furnace use are of high ash and therein lies our chief concern. Among the disadvantages of a high-ash coke are the following:

1. There is less fixed carbon per ton of coke handled.
2. More limestone or dolomite is required to flux it.
3. A high-ash coke will tend to have greater variation and hence the grades of iron will suffer.
4. High ash tends to lower porosity.

We have made several studies of the effects named above, and real progress has been made in correcting some of the faults. Most of the figures used are of practice several years ago, and to the average northern operator will seem very bad. It must be realized that the nature of our burdens with low iron content and high slag volume accounts for a great deal of this. A normal burden would carry only about 35 per cent metallic iron and would yield a slag volume of over 2000 lb. per ton of iron. Nevertheless, we feel that we have made some very tangible improvements in practice in the past few years.

Effect of High Ash on Yield and Cost

The fixed carbon content and the fluxing-stone requirements of coke have a direct bearing on cost. Let us consider the effect of a 2 per cent reduction in coke ash. The first two columns of Table 1 give the figures for an average burden in a certain month. If the coke ash

were reduced 2 per cent this would mean, roughly, a 2 per cent increase in fixed carbon, and hence the furnace could have carried more burden. Distributing this increase in proportion and using enough dolomite to get the same slag ratio gives the figures shown in the last two columns.

TABLE 1.—*Effect of Coke-ash Reduction on Burden*

	Average Burden		Burden with Reduced Ash	
	Pounds	Pounds Iron	Pounds	Pounds Iron
Ore A	8,150	2,720	8,474	2,830
Ore B.. . . .	4,330	1,555	4,509	1,620
Ore C.....	6,130	2,780	6,375	2,900
Dolomite	3,430		3,242	
Total.. . . .	22,040		22,600	
Scrap... . .		595		595
Pounds iron per charge . . .		7,650		7,945
Tons iron per charge		3 42		3 54
Coke unit		9,250		9,250
Number charges per month.. .		2,880		2,880
Tons per charge.....		3.42		3.54
Monthly tonnage.		9,833		10,215
Coke per ton iron		2,707		2,607

This is a saving of 100 lb. of coke and $53\frac{1}{4}$ lb. of dolomite per ton of iron produced. The increased tonnage would mean a reduction in overhead per ton of iron. Assuming that coke costs \$2.00 per ton, dolomite \$0.80 and that overhead is \$1.75, it would be possible to save \$0.100 per ton on coke, \$0.019 on dolomite and \$0.070 on overhead, or \$0.189 per ton of iron, which would amount to \$1930 in the month. On higher grades of ore the saving would be greater, of course, and on higher production the saving in dollars per month would pay for considerable expense to reduce the coke ash.

Effect of Coke Ash on Silicon Control

Another important reason for desiring close control of coke ash is its effect on the silicon in the pig iron. The higher the ash, the more room there is for variation. Thus consider a coke of approximately 14 per cent ash. This might easily vary from 13 to 15 per cent and frequently will if proper care is not exercised. On the other hand,

a coke of 4 per cent ash would vary in the same proportion from 3.71 to 4.29 per cent. Since fixed carbon varies roughly inversely to the ash, with a 10,000-lb. coke unit there would be:

$10,000 \times 2 \text{ per cent} = 200 \text{ lb. carbon variation,}$
 and $10,000 \times 0.58 \text{ per cent} = 58 \text{ lb. carbon variation.}$

Assuming a burden ratio of 2.25:

$200 \times 2.25 = 450\text{-lb. burden,}$
 $58 \times 2.25 = 130\text{-lb. burden.}$

Obviously a change in the burden of 450 lb. is much more deleterious to the furnace than a change of 130 lb., but this is what happens when the coke ash changes.

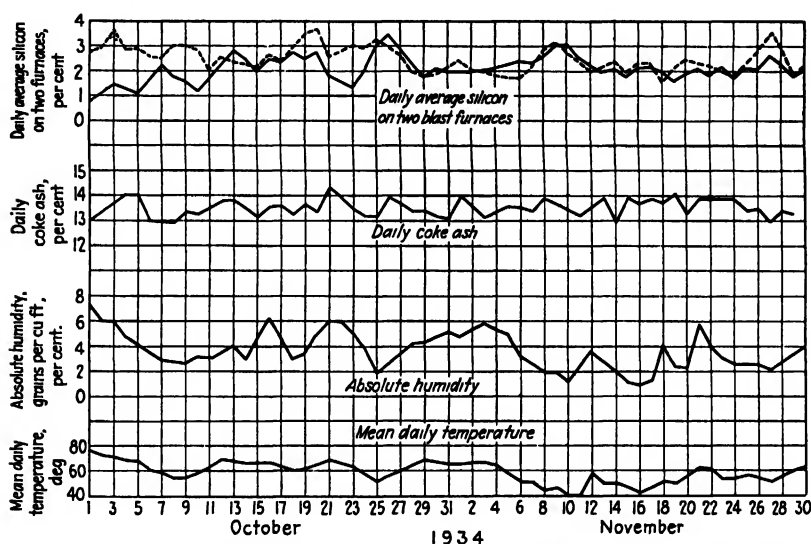


FIG. 1.—VARIATIONS IN SILICON ON TWO BLAST FURNACES FOR TWO-MONTH PERIOD.

That variations in coke ash have an effect on the silicon in the iron has been shown by Johnson¹. The chart in Fig. 1 is interesting as corroborative testimony to his paper. This shows the average daily silicon of two furnaces that had nothing in common but coke and the weather. All ores for each furnace were drawn from separate bins. In general entirely different brown ores were used. The hard ores were from the same mines, but in separate bins, and generally are very uniform.

The silicon on the two furnaces varies in unison. During early October, when one furnace was making basic and the other foundry iron,

¹ H. W. Johnson: Effect of Variations in Coke Ash on Pig Iron Analysis. *Trans. A.I.M.E.* (1933) 105, 28.

the furnaces get hot and cold together, and when both furnaces are on the same general grade the effect is striking.

It might be argued that this is caused by the weather, which we all know has its effect on operation. However, October and early November are usually mild months in the South and the temperature is quite uniform and, as shown on the chart, the absolute humidity, especially during early October, has a uniform trend, while the silicons and ash are varying.

In interpreting the chart it must be remembered that there is considerable lag between the screening station where the coke is sampled and the tuyeres where the effect is felt. The chart was made several years ago in a study to improve furnace control. One of the major advances in recent years has been much closer control over the silicon, and a chart similar to this one for a more recent period would not show the variations in silicon or coke ash.

Porosity of Coke

Coke porosity is a very important feature of satisfactory furnace operation. When the porosity of our coke was increased from about 44 or 45 per cent to 48 per cent we had a marked improvement in practice. Flue-dust losses were lower, grades were better, and coke consumption was materially improved. Undoubtedly this is due to better space-rate of combustion² and to more efficient gas-solid contact.

Here again we have a very important function of the ash, for by reducing the ash you may improve your porosity. Fig. 2 shows the coke ash plotted against the porosity for a period of about a month. The trend curve indicates that a reduction of 2 per cent in the ash will improve the porosity by more than 3 per cent.

Fig. 3 brings out the simultaneous variations of the ash and the porosity quite clearly. Notice that the coke ash is plotted on an inverted scale; i.e., the higher the line, the lower the ash. This shows clearly that the lower the ash, the higher the porosity. Oven operation is important in the control of porosity, but for a given operation the ash is apparently the controlling factor. Hence reduction of ash is important in the control of porosity.

Effect of Coke Size

The sizing of coke, like the sizing of ore, is an important factor in furnace operation. During the depression it was frequently necessary to use in the furnace all coke that was not sold commercially, with the result that at times only one size was available for the furnace, while at

²T. L. Joseph: Behavior of Coke in the Blast Furnace. Amer. Iron and Steel Inst. (October, 1927).

others all sizes except breeze had to be used. A study of this period, therefore, gives an idea of the results of this practice. The figures of

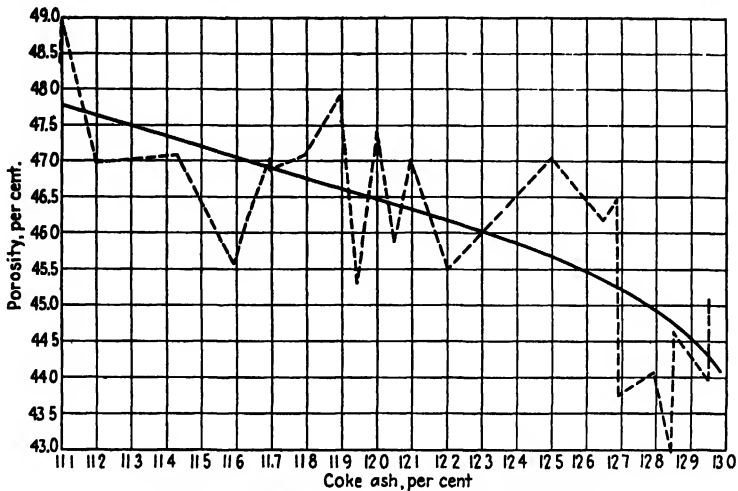


FIG. 2.—EFFECT OF COKE ASH ON POROSITY.

Table 2 are furnace months arranged in the order of increasing coke consumption. The latter figure will look very high to the northern operator. It is accounted for by our large slag volume (about 2000 lb,

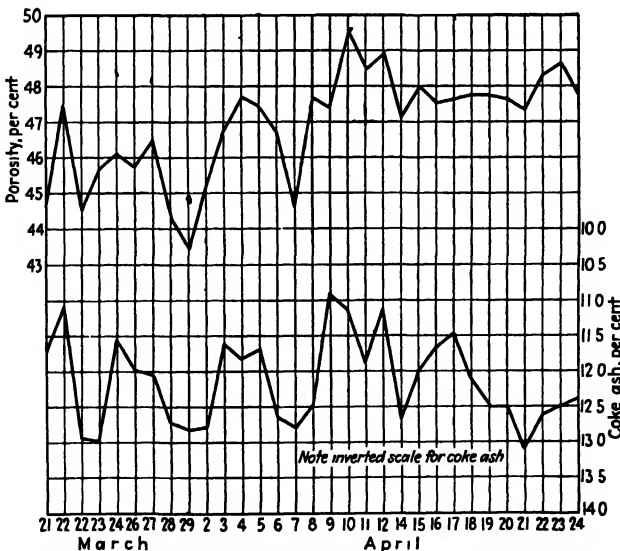


FIG. 3.—VARIATION IN POROSITY AND COKE ASH, BY DAYS.

per ton of iron) and the low percentage of iron in the burden (about 35 to 40 per cent), but owing to the recent improvements these figures have been lessened by 300 or 400 pounds.

TABLE 2.—*Effect of Coke Size*

Hot Blast	Wind	Silicon, Per Cent	Coke Consumption, Lb.	Number of Coke Sizes	Coke Ash, Per Cent
1,170	38,700	2.54	2,707	1.5	14.17
1,135	38,700	2.42	2,712	1 75	14.16
1,250	35,700	3.92	2,742	1.0	13.88
1,170	36,500	2.20	2,742	2.33	13.86
1,225	40,800	2.53	2,790	3 00	14.40
1,200	36,500	2 28	2,795	1.0	13.88
1,170	36,100	2.10	2,826	2.33	13.86
1,190	36,900	2.34	2,850	3 33	14.04
1,280	39,700	2.41	2,859	2.5	13.78
1,180	36,500	2.26	2,891	4 0	13.56
1,175	38,500	2.35	2,894	2.5	13.77
1,170	40,800	2 34	2,939	3.0	14 40
1,220	39,400	2 47	3,002	2 33	13 78
1,220	36,800	3 21	3,016	4.0	13.56
1,175	33,500	2 40	3,033	4.0	13.96
1,070	36,800	2.49	3,259	3 33	14.04

This table makes it clear that when a sizing effect is obtained by charging only one or two sizes the results are much better than when all sizes are mixed together. By crushing coke to proper size and charging one size only to the furnaces, we have greatly reduced our coke consumption in the past year, so that a figure of about 2200 would be more representative.

It is unfortunate that the mechanical layout of our stock house does not permit us to rescreen the breeze from the coke before it enters the skip, as undoubtedly even further savings could be effected, as indicated by experience in other places.

Improvement in Coke in Past Few Years

Two major improvements in coke preparation in the past few years have been:

1. Reduction of coal ash by improved washing.
2. Pulverization of coal before coking.

There is nothing fundamentally new in either of these developments, but considerable time and money have been spent on improving the coke by these two methods.

The necessity for low ash and uniform ash has already been pointed out. We have recently been able to reduce our coal ash by 1.5 per cent by the installation of new jigs at the mines. This is a coal-mining problem but is one that affects the furnaceman.

Very careful control of the washing operation is essential if good results are to be obtained. The coal should be crushed to a fine size in

order that the washing operation may have opportunity to separate the bone and the slate. Depth of beds and angle of bed bottom are matters of great importance, and the proper regulation is found only through constant trial with very close checking of results, for every coal has a different action. A float control is provided, which regulates the feed of coal automatically. The chief problem in this operation is not *low* ash alone, but *uniformly* low ash together with a reasonable washer loss.

Pulverization of coal before it enters the ovens has been introduced to blast-furnace coke plants during the past few years. Its advantages are:

1. Breaking up of the particles of bone and slate reduces the possibility of cross fracture, because of the difference in rates of expansion and contraction between these particles and the coal. If the foreign particles are small enough, there is less opportunity for them to start shrinkage cracks, or other zones of weakness.

2. The pulverization results in a more intimate mixture of the coal and, all the coal being small, there is less opportunity for size segregation and hence there is a more uniform heat exchange in the oven, which results in more uniform structure of the coke.

3. Pulverization, oven heats, and ash are the controlling factors in porosity control.

We use a rotary hammer mill for pulverization, and from 60 to 80 per cent of the product will pass through a $\frac{1}{8}$ -in. screen, depending on operating conditions, coke desired, etc. The improvement in coke structure made by coal pulverized so that 76 per cent goes through a $\frac{1}{8}$ -in. screen, the remainder through a $\frac{1}{4}$ -in. screen, over the same coal simply crushed through $\frac{3}{4}$ in. is indicated by Table 3.

TABLE 3.—*Improvement in Coke Structure by Use of Pulverized Coal*

Tests of Structure	Crushed Coal	Pulverized Coal
Shatter test, per cent.....	70.50	82.00
Tumbler test, per cent:		
Strength.....	113.65	171.66
Hardness... ..	70 75	77 25
Brittleness	73.75	25.50
Fuel value.	131.07	194 40

ORES

As pointed out by Furnas and Joseph², the proper sizing of ores is very important in furnace operation on account of distribution and

² C. C. Furnas and T. L. Joseph: Stock Distribution and Gas-Solid Contact in the Blast Furnace. U. S. Bur. Mines *Tech. Paper* 476 (1930).

gas-solid contact. Sizing of ores to two or three sizes and charging separately into the furnace is being done by two or three southern companies, with admirable results. Although our company has not gone quite so far, nevertheless we are crushing all our hard ores in a crusher set to $\frac{3}{4}$ in. This gives the effect of sizing, only one size being used and that one small. This has greatly improved our practice.

While all the Red Mountain hard ores come from the same vein, there is an appreciable difference in the ore from different mines on the mountain. Thus two ores from opposite ends of the mountain will have analyses approximately as follows:

	Fe	SiO ₂	Al ₂ O ₃	CaO	MgO	P	Mn
West end.	33.78	11.05	3 31	19.32	0.70	0.30	0.16
East end	35 89	23 19	3 25	10.79	0.70	0 32	0.16

The trend of increased iron and silica and decreased lime from west to east holds true the length of the mountain; and the difference does not end there, for the east ore is very difficult to reduce in the furnace, requiring considerably more coke than any theoretical calculations would indicate, and usually causing irregular operation of the furnace. Crushing this ore as fine as $\frac{3}{4}$ in. has greatly improved this situation and we are now able to carry as much as 25 per cent with no bad effects. Undoubtedly this is due to better gas-solid contact in the furnace.

Proper sizing of brown ores is also necessary, and this must be watched more carefully than ever since sizing the hard ore. Most washed ores are usually well prepared, but screened ore frequently is in very large lumps unless great care is taken to see that these lumps are broken up. The effect of large lumps with the finely crushed hard ore was brought out strikingly by a recent experience.

The furnace had been on good grade and operating nicely for a considerable period. It became necessary to make some iron with phosphorus a little higher than normal, and to make this required only the substitution of a high-phosphorus brown ore for the usual low-phosphorus ore. The brown ore constituted about 20 per cent of the burden, but the insoluble was the same in both ores, so that not even a change in dolomite was made. However, this high-phosphorus brown ore was in rather large lumps, ranging roughly from 4 to 12 in. This ore rolled to the center of the furnace on being lowered in and upset the distribution to such an extent that the sulfur went up 15 points, flue dust increased from 69 lb. per ton to 143 and the silicon was impossible to control, finally becoming over 4 per cent. By merely resuming the use of the usual brown ore, we were able to straighten out the furnace. Lumpy ore had been used frequently before, but this was our first experience with a large amount since the finer crushing of the hard ores.

If sizing is to be undertaken, it is necessary to size all raw materials that go into the furnace.

FLUE-DUST CONTROL THROUGH ORE PREPARATION

The past five years have seen much greater interest in flue-dust control in the south. When the cost of ores at the furnace was very low, flue-dust loss was considered a necessary evil, and the operators could not afford to go to any great expense to control it. Higher costs of ore in recent years have altered this viewpoint and now a great deal of time and money is being spent in order to reduce this loss.

The two most important factors in flue-dust control are furnace design and preparation of ores. Furnace design will be taken up later. Screen tests on two hard ores and on flue dust are given in Table 4. Hard ores, as mentioned before, make up the major part of our burdens, and

TABLE 4.—*Screen Tests*

	Ore A	Ore B	Flue Dust
On $\frac{1}{8}$ in	12 59	11 68	1 31
Through $\frac{1}{8}$ in. on 10 mesh	11 14	14 14	5 22
Through 10 on 20 mesh..	26 53	26 37	12 08
Through 20 on 30 mesh	21.83	17 82	20.83
Through 30 on 40 mesh	5.99	6.25	9 10
Through 40 on 60 mesh	11.16	12 86	18 93
Through 60 on 80 mesh	4 52	5 76	19 20
Through 80 on 100 mesh	0.18	0.18	2 60
Through 100 mesh	6 16	5 00	10 73

our flue dust is made chiefly by ore through 10 mesh and on 30 mesh and ore through 40 mesh and on 60 mesh. Thus flue-dust loss could be greatly reduced by screening out all sizes below 10 mesh. To do this on a large scale would be impractical, owing to clogging of screens, etc., so that it would be necessary actually to screen out all ores through a $\frac{1}{8}$ -in. or even a $\frac{1}{4}$ -in. screen. If this were done and the ores used were in the proportion of 15 per cent ore A and 85 per cent ore B, about 28.5 per cent of the ore would be removed. Some means of disposing of this large amount of ore would have to be devised, and it has been suggested that it be sintered, using the already available flue dust, of which there are large stocks in the South, as a fuel. This sinter could then be charged to the furnace with considerable saving of coke if experiences in other places using sinter may be taken as a fair indication.

Crushing and sizing of ores at present probably have some effect on flue-dust control. The properly sized ores work better in the furnace and hence prevent channeling and irregular movements that tend to

increase dust loss. Dust loss has been reduced from around 300 lb. per ton to where 100 looks high, and some plants are getting below 50. It is difficult to determine which proportion of this is attributable to ore preparation and which proportion to furnace design.

FURNACE LINES

Furnace lines have always been a subject of great interest to operators. Fig. 4 shows the changes in lines at one plant from 1928 to March, 1935. Most charts of this kind have always shown changes in the hearth, usually increasing its diameter. This figure, however, shows no changes in the hearth during the entire period, but considerable changes above the tuyeres. After all, this is more or less logical, since the hearth proper serves chiefly as a crucible to store the iron, from which it may be removed at more frequent intervals as the tonnage increases, while the portion of the furnace from the tuyeres to the stock line is where the real work is done.

The general tendency in this chart is towards a steep bosh angle and an increase in stock-line diameter, especially the latter. There is one reversion to the narrow stock line in 1933, but this was due to the desire for a smaller furnace, owing to the small demand for iron at the time. This furnace was not satisfactory as far as flue-dust production is concerned, and there seems to be no doubt that the wide stock line is necessary for effective reduction of dust.

Several important changes in design are indicated in the 1935 lines. The height of the furnace was increased 5 ft. 3 in., primarily as a means of controlling flue dust. If the ore column is the same height in the two furnaces, the taller furnace will have a space of 5 ft. greater distance for the gas to travel and hence give the gas more opportunity to drop dust particles. In other words, this space acts as a primary dust catcher, but the dust returns directly to the furnace and does not have to be rehandled.

Another change is the introduction of the gas passage outside the hanging armor, which may be seen more clearly in the sketch of Fig. 7. One of the chief causes of dust production is the increased velocity of the gas when the bell is lowered, due to a cutting off by the bell of a portion of the available outlet to the offtakes. By the use of the gas-passage space, the effective stock line as far as gas is concerned is 18 ft. 10 in. with an area of 50 sq. ft. that is unaffected by the position of the bell. This large area would give an entirely different distribution of the ores if it were made by simply widening the top, but the hanging armor reduces this area to 17 ft. as far as the incoming ore is concerned.

On this furnace also four uptakes were installed at an angle of 45° in place of the two former uptakes at 90° . Thus the off-take area is doubled, with consequent reduction of gas velocity and hence lower dust loss. The 45° angle is also effective in returning to the furnace the

large lumps of coke ore and scrap that sometimes were thrown out. There is, of course, nothing startlingly new about this design, but Fig. 5 shows this furnace to be of the latest modern design.

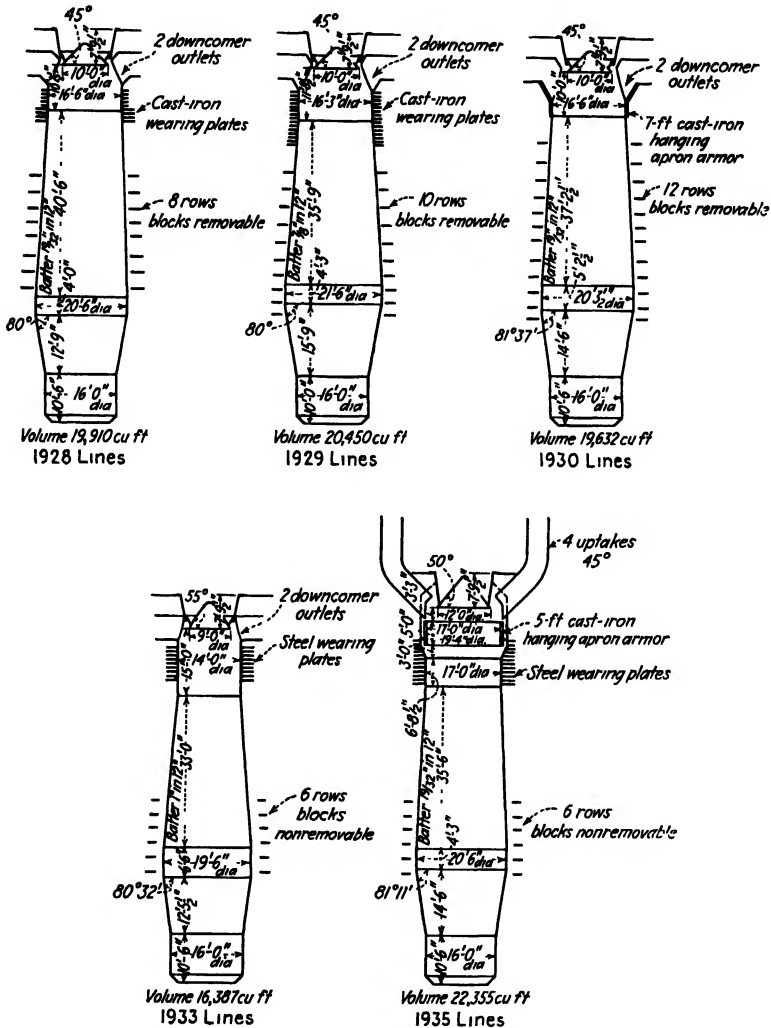


FIG. 4.—FURNACE LINES, 1928 TO 1935.

Another item of interest in this furnace is the installation of examination holes. An extension of the uptake nozzles was brought up close to the receiving hoppers and removable covers placed thereon. It is thus possible to work the furnace down on the rod, take the wind off, open the boxes and safely inspect the condition of the brickwork, armor, filling, and so forth.

Fig. 4 shows that the general tendency has been towards a very steep furnace, with a bosh angle well over 80° and increasingly longer straight section. However, since starting the finer crushing of the ores and using generally smaller but more uniformly sized raw materials of all kinds, there is a strong probability that the next change will be back towards a flatter bosh. The wider stock line seems to be a step in the right direction and apparently it is here to stay.

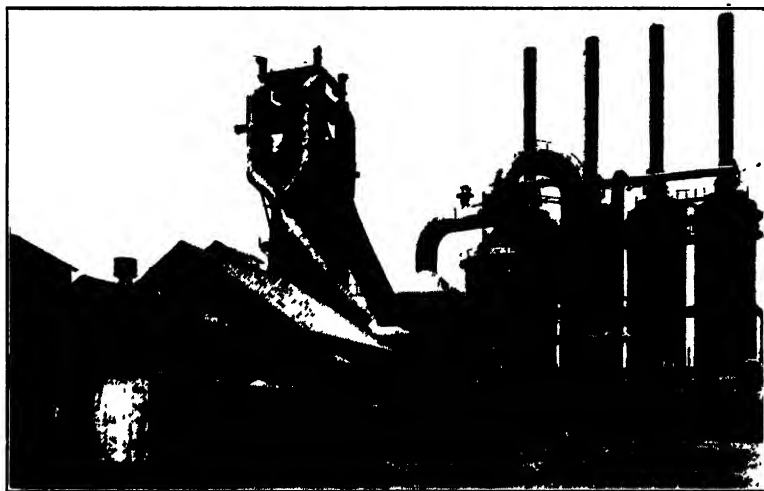


FIG. 5.—No. 2 FURNACE, REPUBLIC STEEL CORPORATION, AT THOMAS, ALABAMA, RECENTLY REMODELED.

NEW BOSH

An important contribution to furnace design has been the development of what is practically a permanent bosh. This bosh is simple in design, yet is very strong and has proved most satisfactory in our five years of experience with it.

As shown in Fig. 6, the main feature of the bosh is a $\frac{7}{8}$ -in. firebox steel plate, which is made up in 12 sections butt-welded by an electric arc to form the circle. A gap of $1\frac{1}{2}$ in. is left at the bottom to provide room for expansion or possible upward movement of the tuyere jacket, and there is a $\frac{1}{2}$ -in. packing space between the plate and the brickwork. Particular attention is called to the design of the block housings. These extend from 4 to 6 in. inside the furnace and form a support for the cooling blocks, thereby eliminating the leverage on the ends of the blocks. The bottom of the housing touches the block only at the ends, and there is a tapered fit at the outside of the housing, so that the blocks can be easily removed when necessary. A keeper is inserted in the projecting lugs, as a safety measure. If it is desired to change the bosh

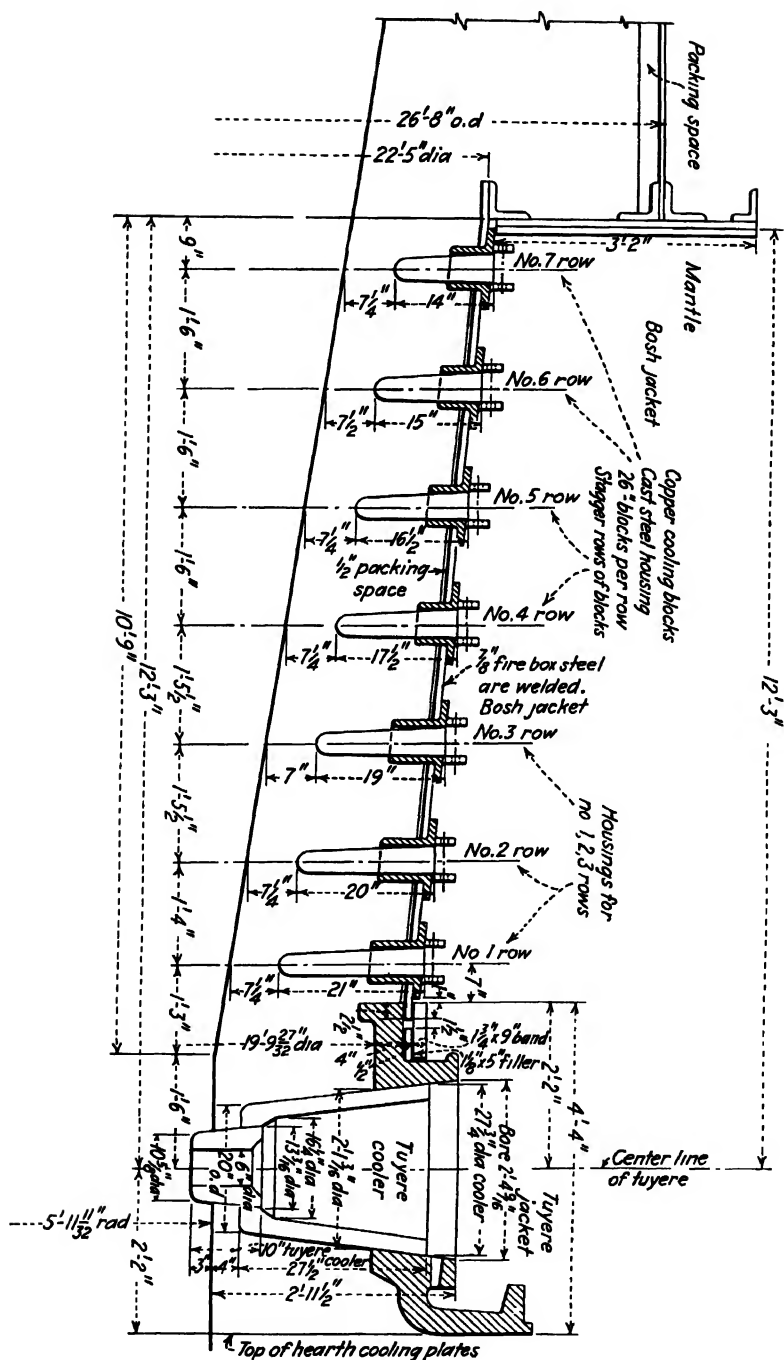


FIG 6.—ARRANGEMENT OF NEW BOSCH.

angle, this may be done by merely changing the length of the cooling blocks.

The permanence of this bosh is shown by the fact that both furnaces have been relined several times since it has been installed but that the bosh has not yet been relined, in spite of the fact that we have made a great deal of 15 per cent ferrosilicon, which is very hard on furnace linings.

DISTRIBUTION

The important subject of distribution has not been forgotten. Most, but not all, of the southern furnaces are now using the McKee distributor. The operation of this distributor is well understood by all furnacemen, so that it is unnecessary to describe it here.

Work has been done by the Bureau of Mines on scale models, on the subject of distribution, but a study that was made on an actual furnace last March may be of interest. The furnace had not been blown in, and before it was lighted off it was filled with coke to a point 24 ft. 6 in. below the bell. We then went inside the furnace and took observations on the distribution. After each lowering of the bell this was repeated until the furnace was full and in this way a good idea of the way the ore and coke tends to fall was obtained. This was more accurate than a scale model, but did not have the effect of the wind going through it. It is doubtful whether this would have any pronounced effect.

The results of this test are shown in Fig. 7, which shows that if the furnace is down on the rod, the ore tends to pile in the center. At about 14 ft. from the bell it flattens out, and from there on up there is a decided cup towards the center. Larger lumps tend to segregate in the middle all the way, showing the normal tendency to an open center.

QUALITY OF PRODUCT

An important development in the past five years in the South has been the marked improvement in the chemical characteristics of the iron produced. No longer is it possible to burden the furnace with whichever ore is most available for use and just to make pig iron. Increased knowledge of metallurgy makes it imperative that the iron produced be within fairly close specifications.

Silicon content must now be held within fairly narrow limits and sulfur *must* be held very low. The various ores used must be properly burdened to reduce the phosphorus content and increase the manganese. This means that higher priced brown ore and manganese ore are an essential part of the burden, and very strict control must be exercised over the furnace to obtain the desired silicon content at all times.

The normal pig iron now produced has phosphorus of about 0.75 per cent as opposed to 0.85 per cent a few years ago, and the manganese

has been increased from about 0.35 or 0.40 per cent to approximately 0.60 per cent. Furthermore, there is an increased demand for pig irons of special analysis, requiring these elements to be much lower or much higher, as the case may be, while still keeping the silicon in a fairly narrow range.

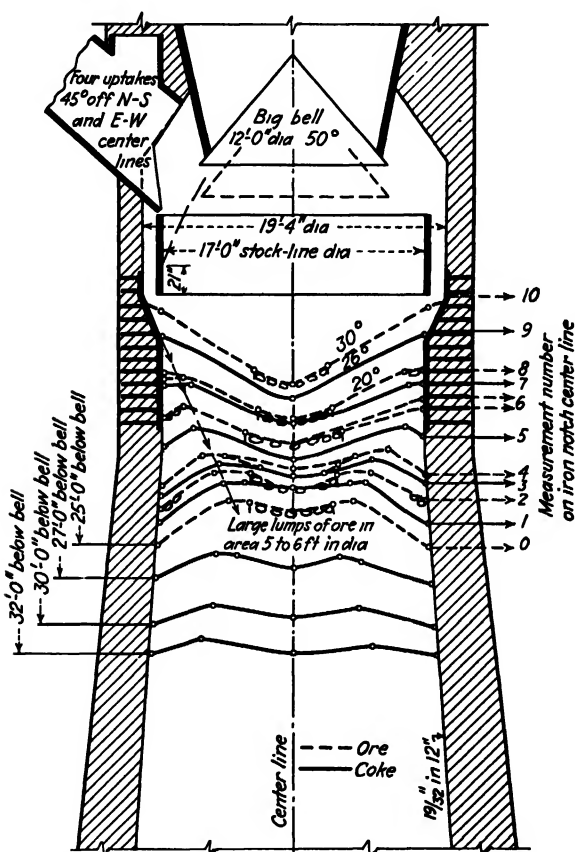


FIG. 7.—CROSS SECTION OF FILLING, NO. 2 BLAST FURNACE, MARCH 2, 1935, REPUBLIC STEEL CORPORATION. BIRMINGHAM DISTRICT.

This cross section is on north-south (Iron Notch) center line. The east-west section is so nearly the same that only one sketch is shown.

All of this requires careful selection and analysis of ores and uniform operation of the furnace.

IMPROVEMENT IN PHYSICAL APPEARANCE

During the past five years more and more emphasis has been placed on the physical appearance of merchant pig iron (Figs. 8 and 9). During

this period, machine-cast iron has entirely displaced the sand-cast. There are many advantages to the consumer as well as to the producer of this type of iron. Lower cost and fewer man-hours appeal to the producer, but improved product appeals to the consumer. A few of these advantages are:



FIG. 8.—PIG IRON OF BAD APPEARANCE, IN 1929.

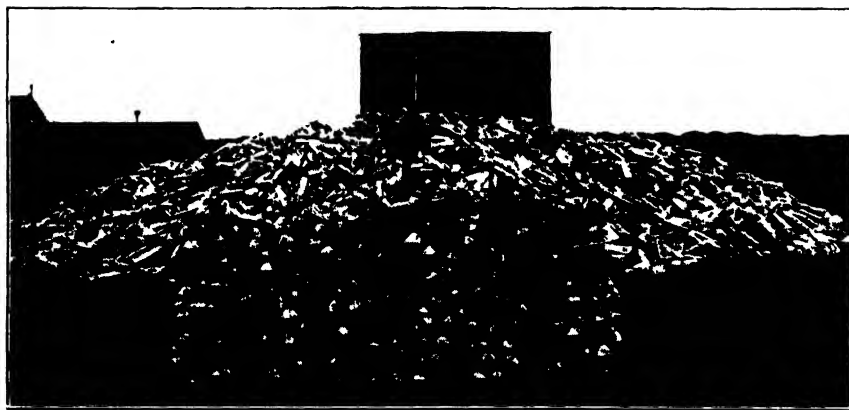


FIG. 9.—GOOD PIG IRON, 1933.

1. Iron is held in the ladle for a while, giving a mixing effect and consequently a more uniform analysis per car.

2. During this period, impurities, such as slag particles, have time to separate from the iron. Occluded gases also have an opportunity to escape.

3. Careful skimming removes most of the foreign matter from the iron when it is poured at the pig machine.

4. The customer buys iron only, and not some adhering sand.

5. Pigs are of more uniform size. There are no sows or jumpers.

Soon after machine-cast iron was introduced in the South, it was found that this iron must have a very finished appearance in order to obtain a market. Scruffy or rough looking pigs were not tolerated, and fracture, while not the means of determining the grades, was still held

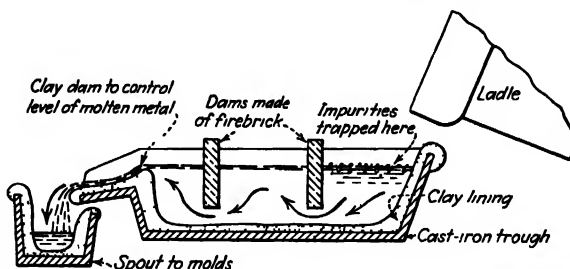


FIG. 10.—POURING TROUGH FOR SKIMMING ON PIG MACHINE.

to be important. There is still a great deal we do not know about fracture, and certain melters have good reason to insist upon the proper type of fracture *as well as* the proper chemical analysis.

The first improvement in machine-cast iron was the introduction of triple skimming. The iron is carefully skimmed at the furnace before going into the ladle. While it is in the ladle certain included impurities have opportunity to rise to the surface, which are removed by two more skimmers as the iron is poured at the pig machine, as shown in Fig. 10, and may be raked off from time to time. A few scruffy pigs are usually

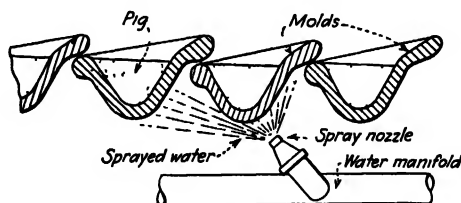


FIG. 11.—WATER SPRAY COOLING MOLD ON PIG MACHINE.

made at the beginning of pouring and these are removed from the car before shipment.

Some customers prefer a more open grain than is usually seen in machine-cast iron, and for this reason we developed a method of slow cooling that gives a fracture similar to that of sand-cast iron. This consists in running the strand fairly slowly, and not putting water on the pigs at the beginning. About 30 ft. from the end of the strand, water is sprayed on the bottom of the molds as shown in Fig. 11. In this way

the heat transfer is from the pig *through* the molds to the water, and hence is much slower. This gives the pigs time to deposit graphite and form the usual fracture. About 15 ft. from the end, water is turned on the top of the pigs to insure complete solidification and absence of bleeders, and to cool the pigs so that the cars will not be damaged by heat. Final cooling is given by water sprays in the car after it has left the molds.

An important feature of the pig-machine operation is the coating or wash on the molds. One of the most satisfactory is a mixture of half pulverized coal and half hydrated lime. Molds are first cleaned by a steam spray, then the facing mixture is sprayed on and the facing is dried by passing over a gas flame. A mechanical brush removes the thick coating at the shoulders of the mold, as this does not always dry thoroughly and is apt to cause boiling of the iron in the mold. This type of wash on the molds gives a very smooth looking pig, similar to any good casting, and helps to eliminate "stickers."

There are many other factors in making a smooth and satisfactory pig. Close watch must be made on the amount of water used both on the strand and in the car, as this is one of the chief factors in determining the rate of cooling, the other being the rate at which the strand moves. The rate of pouring the ladle is also important and must be coordinated with the movement of the chain to make the proper size of pig. If pigs are cooled too quickly they will form a chill and be apt to break on dropping in the car. On the other hand, if they are not cooled quickly enough they will break open and "bleed," changing the weight of the pig, and certainly not adding to the appearance. The weight of individual pigs is of great importance to foundries that charge by bulk instead of weight.

In spite of all these precautions, it is still impossible to make good looking iron if the condition of the furnace is wrong. A furnace that is not moving properly, or the use of badly prepared ores, will change the character of the iron so that all the effort at the pig machine to obtain clean product will be in vain.

CONCLUSION

The major developments in southern blast-furnace practice during the past five years have been:

1. Reduction in ash of the coke.
2. Improved structure and porosity of the coke.
3. Sizing of coke.
4. Sizing of ores.
5. Careful selection of ores from chemical standpoint.
6. Wider stock lines.

7. Improved offtakes and downcomers.
8. Improved bosh design.
9. Widespread use of McKee distributors.
10. Introduction of machine-cast iron.
11. Improvement in physical characteristics of iron.

The statement that any given improvement in practice has been directly due to any one improvement in design has been carefully avoided in this paper. Many things have been done and much good has resulted, but it would not be right to say that reduction of flue dust was due solely to changes in design of the furnace, for proper preparation of ores and coke has surely helped. So it is on coke consumption. A summary of the improvements in practice is therefore in order:

1. Coke consumption has been reduced from around 3000 lb. per ton or higher to about 2200 or 2300.
2. Flue-dust production has been reduced from 250 or 300 lb. per ton of iron to between 50 and 100 lb.
3. Chemical analysis of the iron has been improved.
4. Furnaces are kept more uniformly on the desired grades.
5. Man-hours have been lowered through mechanization.
6. Physical appearance of the iron has been greatly improved.

ACKNOWLEDGMENTS

In conclusion, I wish to thank Mr. C. L. Bransford, Mr. W. E. Curran, Mr. T. J. Carpenter and Mr. J. M. Hassler, whose suggestions and criticisms were most helpful in preparing this paper, and Mr. W. M. Stewart, Mr. H. J. Simpson and Mr. J. M. Hassler for assistance in preparing the charts and diagrams—all with the Republic Steel Corporation, Birmingham District.

DISCUSSION

(S. P. Kinney presiding)

C. L. BRANSFORD,* Birmingham, Ala.—Many of the points brought out in this paper are old to many operators, but they are new to us. When I began work with Republic Steel in 1929, there were approximately 60,000 tons of pig iron on the ground that could not be sold. The other companies selling merchant iron had the market because they were making sand-cast iron. We were told that Republic iron would not sell because the analysis was not right; that the sulfurs were held too close to 0.05 per cent. The company was making an iron that in appearance was gray forge iron, although there was perhaps 2 to 2.5 per cent silicon in it. The result was we had no market.

As soon as we adopted triple skimming and the slow cooling of pig iron, and improved our furnace practice, we had a good sale for our pig iron; in fact, we began to sell more than our competitors. Now the other companies in the Birmingham district are doing just what we are doing.

* Assistant District Manager, Republic Steel Corporation.

As Mr. Crockard said, we feel that much improvement has been made in the sizing of our ores. Fifteen years ago the thought of crushing hard ores down to $\frac{3}{4}$ in. and under would have seemed foolish; now we are not only crushing the ores, we are also sizing our coke. I think the top screen on coke is set at 3 in. and the bottom screen at 1 in. That has been a great improvement. We intend to go still further, and make three sizes out of the hard ore, believing that it will bring about improvement. Our idea is to take the $\frac{1}{4}$ -in. and lower to sinter with the flue dust that is in stock—probably some 800,000 tons. Other companies are sizing their hard ores in two sizes.

The southern furnaces until recently have produced large amounts of flue dust, but I am happy to say that that is decreasing. One company in the Birmingham district boasts a figure of about 22 lb. of flue dust per ton of iron. That is almost unbelievably low, but that company has proved that it is right. Ours is under 100 lb.

There is not a sintering plant in the South for sintering flue dust, for the reason that until the last five or six years the ores have been so cheap it was not profitable. Even with the present high labor rates, however, the Republic Steel Corporation can figure a profit on it.

It is only within the last three or four years that we have gone into widening tops. Another southern company was the pioneer, and the remainder have almost all followed suit.

Separation of Hematite by Hysteretic Repulsion

BY E. W. SCHILLING* AND HARWICK JOHNSON†

(Chicago Meeting, October, 1935)

THE separation of hematite by hysteretic repulsion was first brought to the attention of the public in 1922, by W. M. Mordey¹. Three years later another paper² was published and after another four years a third paper³ appeared in the South African publications. Certain data were lacking in these papers. In order to continue the work intelligently a knowledge of the shapes of the hysteresis curves for certain minerals was very necessary. This information was not available until the present year⁴. It was known that reduction of certain ores rendered them amenable to this process of separation but definite data in the form of curves showing exactly the effect of such treatment were lacking. Probably our best source of information on the separation of minerals by the use of alternating-current magnetic fields today is the reports from the U. S. Bureau of Mines⁵⁻⁷.

It is not the purpose of this paper to tell the reader in detail how to make a commercial separator. Experimental models have recently been made⁷ and the results obtained have been so good that it is the opinion of the authors that the public will soon take an active interest in the subject and its development. The writers have constructed a separator that is considerably different in construction and operation from the two types described by Mr. Davis. This will be described, but the real purpose of this paper is to outline certain experiments and give curves showing data that have a fundamental bearing upon the practical construction of a separator of this type.

Specular hematite is usually considered nonmagnetic; that is, it is very feebly magnetic as compared to some other minerals. If specular hematite is placed in a steady magnetic field there is no apparent attraction. At the moment of closing the switch, however, some particles may be seen to move. If the field is alternating, the particles are con-

Manuscript received at the office of the Institute June 25, 1935; revised August 22, 1935.

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† Research Engineer, Michigan College of Mining and Technology.

¹ References are on page 71.

tinually in motion, being repelled from the pole piece. Reduced hematite has very low remanence and very high coercive force⁵, which means that as the field reaches zero the remanent magnetism is small but the amount of negative field necessary to reduce it to zero is large. Hence, when the field reverses the magnetized particles are lined up in the wrong direction for attraction and are repelled. Therefore, the amount of repulsion is dependent upon both coercive force and remanence. Mordey has used the term "hysteretic repulsion" in referring to these two characteristics, which govern the activity of hematite in an alternating magnetic field. The name seems very appropriate and is therefore used throughout this discussion.

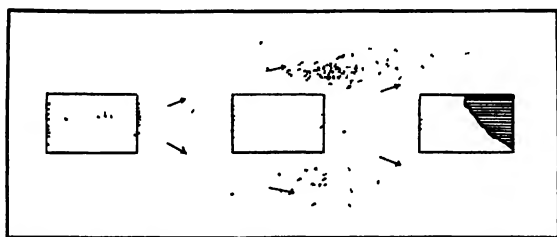


FIG. 1.—MOVEMENT OF SPECULAR HEMATITE OVER A THREE-PHASE THREE-POLE MAGNET.

It has been found that alloying, heat-treating, or mechanical work has little effect upon the remanence of iron but the coercive force may be greatly affected⁵. This explains the fact that, although normally red hematite shows no activity in the alternating field, after heat-treating at 500° C. in an atmosphere of hydrogen and magnetizing with a direct-current field, some particles jumped into the air as high as 2 and 3 inches.

EFFECT OF POLYPHASE ALTERNATING MAGNETIC FIELDS UPON SPECULAR HEMATITE

A three-pole magnet, as indicated in Fig. 1, was used in the polyphase tests. Specular hematite was placed over the left-hand pole in Fig. 1. The movement of the specular hematite was towards the right and away from the line of poles as indicated by the arrows. Approximately 55 per cent of the material was repelled from within $\frac{1}{2}$ in. of the pole pieces. Some of the material formed small pyramids at the left-hand edges of the pole pieces, indicating the presence of magnetite. A few particles were repelled from the left-hand pole towards the left. Three-phase excitation was used, the three coils being connected in delta. The movement along the line of poles could be reversed by changing the phase rotation.

A $\frac{1}{4}$ -in. brass plate of elliptical shape was placed over the right-hand pole. The effect of this shown in Fig. 2 was to increase the lateral repulsion away from the line of poles. The repellent effect of the brass plate was so great that very few particles remained over it. Under this condition 70 per cent of the material was repelled from within $\frac{1}{2}$ in. of the pole pieces.

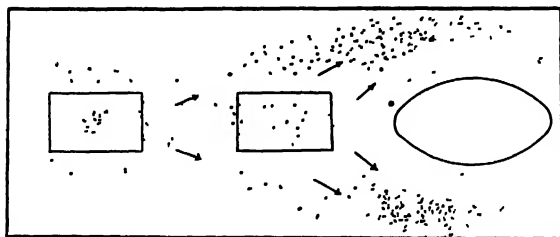


FIG. 2.—EFFECT OF A $\frac{1}{4}$ -IN. ELLIPTICAL BRASS PLATE PLACED OVER ONE POLE.

A $\frac{1}{2}$ -in. aluminum plate was placed over the entire magnet as shown in Fig. 3 and specular hematite was placed over it upon a glass plate. The effect produced is shown in Fig. 3. A strong lateral repulsion repels about 70 per cent of the material from the area directly over the plate. The longitudinal movement along the line of poles was very slight.

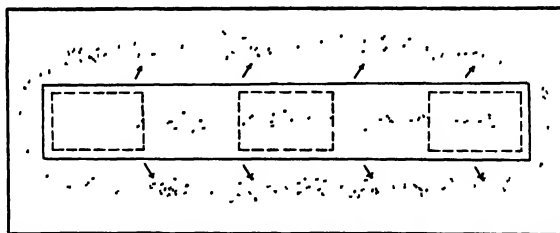


FIG. 3.—EFFECT OF PLACING A RECTANGULAR ALUMINUM PLATE OVER THE THREE POLES.

Using two-phase excitation and two poles of the magnet, the effects are generally similar to the effects with three-phase excitation.

EFFECT OF AIR GAP

As the air gap between the plane upon which the specular hematite is supported and the iron core of the magnet is varied from a value at which the movement of the hematite ceases, a value is found at which the activity of the particles is maximum. The distance of the lateral movement increases with the air gap until a certain value of air gap has been reached, and from there on it decreases. The longitudinal movement along the line of poles increases until a certain optimum value of the

air gap has been reached, thereafter it decreases but not as rapidly as the lateral movement. This makes the longitudinal movement more evident at the higher values of air gaps, although in reality it has been decreased. The curves of Fig. 4 shows the relation between the length

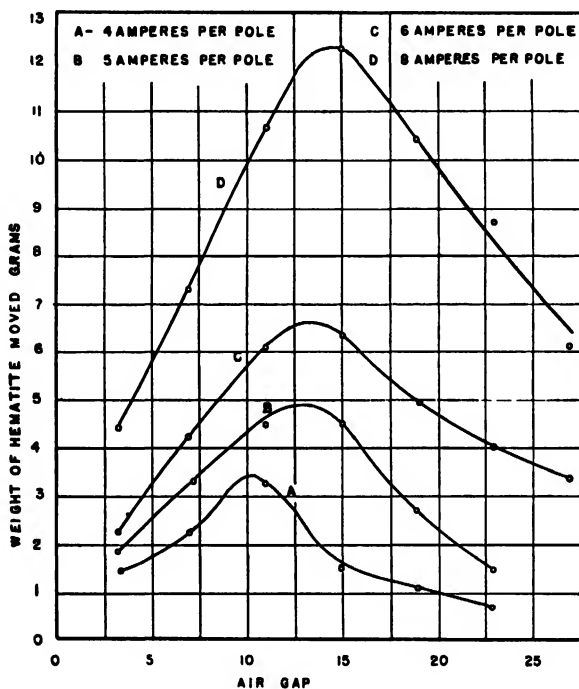


FIG. 4.—EFFECT OF LENGTH OF AIR GAP.

of air gap and the amount of hematite separated for various values of excitation.

EFFECT OF FREQUENCY OF EXCITATION UPON SPEED OF MOVING PARTICLES

To determine the effect of the frequency of the alternating magnetic field upon the speed of the moving particles of specular hematite, the frequency of the three-phase excitation was varied and the average speed of the particles traveling between the inner edges of the outer poles (10 in.) was measured. The coils were wye-connected, using an excitation of 10 amp. per pole throughout the test. The supporting surface was suspended from a pipe frame by cords, to absorb vibration. The air gap was $\frac{3}{8}$ in. over each pole. Data were taken and plotted in Fig. 5.

EFFECT OF VIBRATION UPON WEIGHT OF HEMATITE MOVED

In attempting to obtain data for a curve between the amount of hematite moved in a given time and the excitation, it was found that as the excitation was increased a certain amount of vibration was being introduced into the plate. Therefore it became desirable to measure the extent of this vibration, to be able to vary it in known amounts or to keep it constant as desired. The amplitude of the vibrations were relatively measured by means of a dynamic microphone driven directly by the vibrating surface. The output of this microphone was passed through an amplifier and the voltage measured with a vacuum-tube

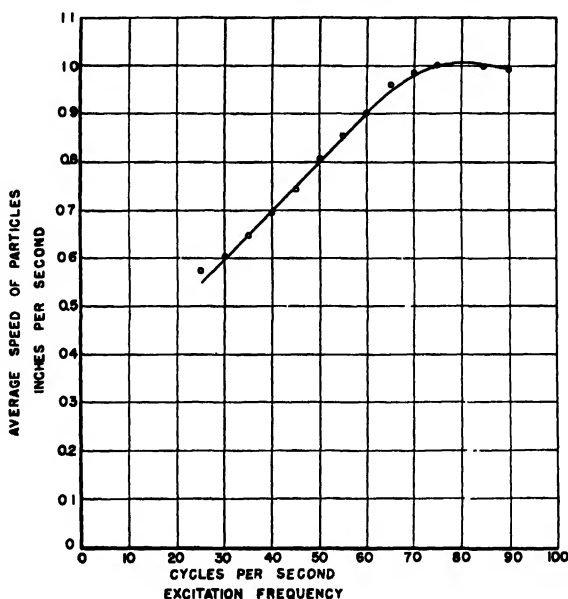


FIG. 5.—EFFECT OF EXCITATION FREQUENCY UPON SPEED OF MOVING PARTICLES.

voltmeter (Fig. 6). The vibrations were introduced by means of a separate magnet. This was a two-pole magnet excited by a single-phase current. An iron plate was placed on top of the magnet with the glass plate resting upon it. The amplitude of the vibrations was varied by regulating the excitation of the two-pole magnet with an induction regulator. The glass supporting surface was suspended level with an air gap of $\frac{5}{8}$ in. over pole No. 1 and $\frac{3}{4}$ in. over pole No. 3.

At the beginning of each trial, the amplitude of the vibration was adjusted to the desired magnitude, about 60 grams of material was spread evenly over pole No. 1 and the excitation was applied. After five minutes the excitation was cut off and the hematite that had moved was collected and weighed. This was repeated for various ampli-

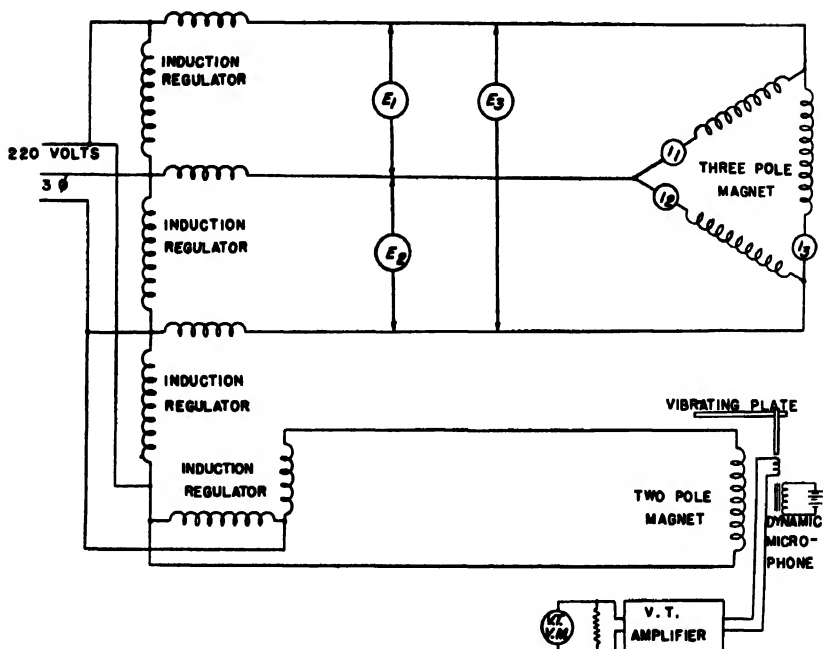


FIG. 6.—APPARATUS FOR CONTROLLING AND MEASURING VIBRATION

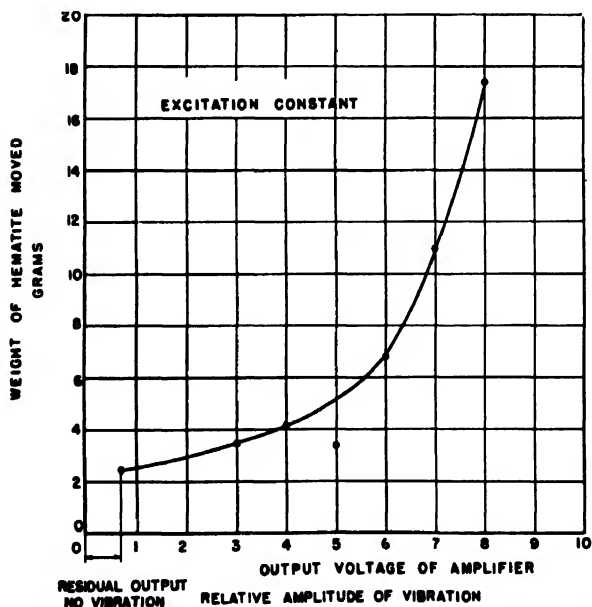


FIG. 7.—EFFECT OF VIBRATION UPON WEIGHT OF HEMATITE MOVED.

tudes of vibration. From the data thus secured the curve of Fig. 7 was produced.

EFFECT OF CONSTANT VIBRATION UPON EXCITATION-TEST CURVES

The vibration of the supporting surface was induced by the use of an auxiliary magnet, as previously explained. It was maintained at a constant value by means of an induction regulator varying the excitation of the auxiliary magnet.

The shielding around the microphone unit was not adequate to exclude all inductive pick-up, and it was necessary first to apply the excitation to the auxiliary magnet and adjust the vibration each time

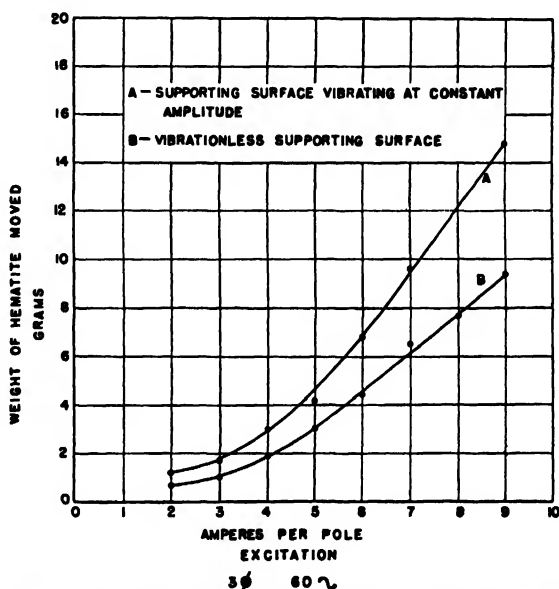


FIG. 8.—EFFECT OF CONSTANT VIBRATION UPON EXCITATION TEST CURVES.

so that the output voltmeter of the amplifier read a constant value above that reading without the auxiliary magnet being excited. This kept the vibration of the supporting surface at a constant amplitude.

The supporting surface was level with air gaps of $\frac{5}{8}$ in. over No. 1 and $\frac{3}{4}$ in. over pole No. 3. A brass plate was used over No. 3.

An excitation test under the same conditions, except that the supporting surface was vibrationless, was also run for comparative purposes.

The output of the amplifier was maintained 2.1 volts above the amount induced from the three-phase circuits. The amplitude of the vibrations was quite small, so that uniform readings could be made at the higher values of excitation. The curves for this test are shown in Fig. 9.

HEAT-TREATMENT

A study of specular hematite was made with respect to changing its magnetic properties by reduction of the hematite. This was done by reducing the oxygen content through heating in an atmosphere of hydrogen. An electric furnace of which the temperature could be accurately controlled was used to heat the material to the desired temperature. The treatment consisted of heating the material while hydrogen was passing over it, to 500° C., maintaining the temperature at this value for 30 min., continuing the flow of hydrogen, and then allowing the material to cool in hydrogen.

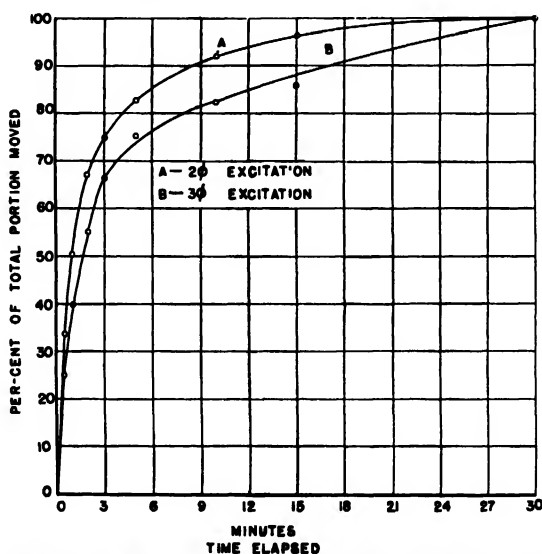


FIG. 9.—COMPARATIVE TWO-PHASE AND THREE-PHASE EXCITATION TESTS.

The treated material exhibited magnetic properties, being attracted to any magnetic object. When some of the treated specular hematite was placed in an alternating field, the particles were very active, being repelled rapidly from a strong field. Its activity was much greater than before treatment. When the alternating field was removed, it was observed that the particles had become magnetized, adhering to each other and presenting an appearance similar to wet sand. When tested in a steady field the treated material exhibited strong magnetic properties, being attracted to the field and forming pyramids over the pole pieces.

An interesting phenomenon developed when treated material that had been magnetized with direct current through the magnets was subjected to an alternating field. It became extremely active, very much more so than before it was magnetized.

Field excitation tests were made to obtain data from which to compare the speed of movement of specular hematite under four conditions: (1) no treatment, (2) heat-treated at 350°C ., (3) heat-treated at 500°C ., and (4) heat-treated at 500°C . and magnetized. Curves showing the results of these tests are to be found in Fig. 10.

With untreated specular hematite the adjustment of the air gap was not critical but with the treated material it was. The air gap was kept the same for the three curves of Fig. 10. It was the distance that was best for untreated hematite.

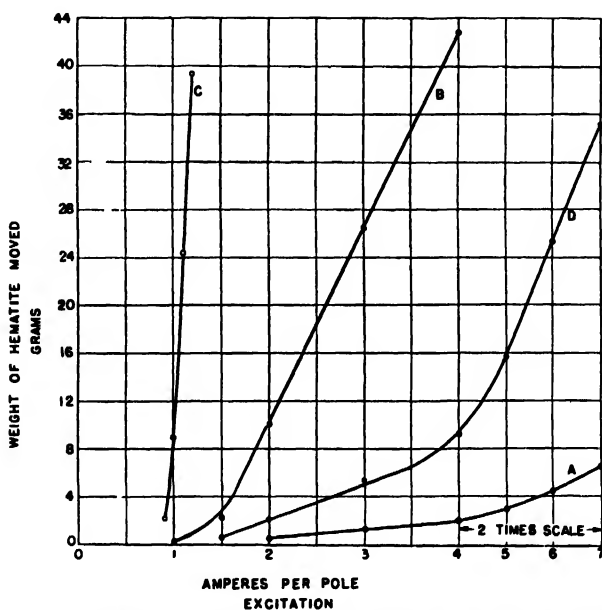


FIG. 10.—EXCITATION TEST CURVES OF SPECULAR HEMATITE SHOWING EFFECT OF HEAT-TREATMENT IN A REDUCING ATMOSPHERE OF HYDROGEN.

- | | |
|--|--|
| A. Untreated. | C. Heat-treated at 500°C . and magnetized. |
| B. Heat-treated at 500°C . | D. Heat-treated at 350°C . |

INVESTIGATION OF RED HEMATITE

A sample of low-grade red hematite was investigated to determine the effect upon it of an alternating field. The sample was crushed fine (about 20 mesh) and placed in the field. This sample was practically unaffected by the field. When the specimen was placed in a steady magnetic field, some of the particles adhered to an iron object brought into contact with them. The particles were not attracted by the field. These tests show the very weak magnetic character of red hematite.

The hematite was then given the same heat-treatment that had been given to the specular hematite, and tests were again made to determine the reaction of this heat-treated red hematite to steady and

alternating fields. In an alternating field most of the particles were quite active, in that they were constantly in motion. This consisted mainly in vertical jumping motion over the poles, some of the particles jumping as high as 2 or 3 in. The repulsion from the poles was not as great as would be expected from the activity of the particles.

Many of the particles, like magnetite, would move out to the edge of the pole piece and there form pyramids. If a metallic iron object was brought near to the particles in an alternating field, the particles were attracted to it quite violently. As soon as the alternating field was cut off the particles lost their magnetic properties.

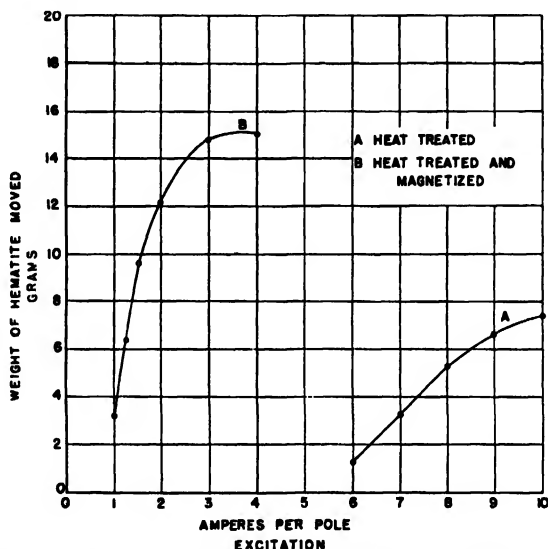


FIG. 11.—EXCITATION TEST OF RED HEMATITE, SHOWING EFFECT OF HEAT-TREATMENT IN REDUCING ATMOSPHERE OF HYDROGEN AND SUBSEQUENT MAGNETIZING WITH DIRECT CURRENT.

Curves are shown in Fig. 11. Untreated red hematite was unaffected by the alternating field, hence no curve appears for this condition.

AN EXPERIMENTAL SEPARATOR

A laboratory model separator has been built, bearing in mind information gained from previous tests. It was shown that the separation was materially aided by giving the ore a preliminary direct-current activation. A direct-current magnet was therefore incorporated as a part of the equipment. It will be noticed (Fig. 12) that the magnet is above the main conveyor belt. A cross belt moving slowly serves to carry any magnetic material off to the side. This is important when the ore contains magnetic material in addition to the hematite. A polyphase magnetic field is used for activation with the alternating current. By

causing the field to travel in a direction opposite to that of the belt less concentrate is carried over into the tailings. This machine has only recently been completed and quantitative data are not yet available.

CONCLUSION

There seems to be little doubt concerning the effectiveness of this kind of separation. As to how soon it will receive commercial application will doubtless depend upon its further perfection and upon the economics of the situation. It would seem that an article on this phase of the subject would be a welcome addition to the literature at this time.

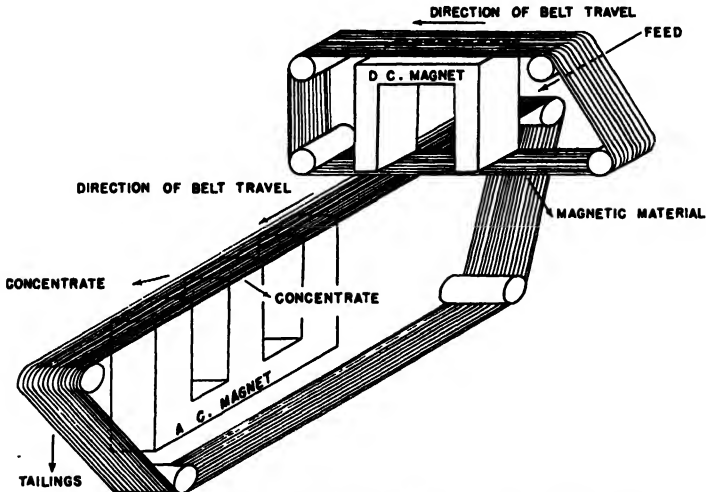


FIG. 12.—SCHEMATIC DIAGRAM OF EXPERIMENTAL SEPARATOR.

ACKNOWLEDGMENTS

The writers are indebted to the Metallurgy Department of the Michigan College of Mining and Technology for the liberal supply of ore. They are also indebted to Prof. G. W. Swenson, Head of the Department of Electrical Engineering, for his cooperation as well as numerous suggestions.

DISCUSSION

(*R. F. Harrington presiding*)

R. S. DEAN* AND C. W. DAVIS,† Washington, D.C. (written discussion‡).—There seems to be some confusion concerning the action of magnetic particles under the

* Chief Engineer, Metallurgical Division, U.S. Bureau of Mines.

† Associate Chemist, U.S. Bureau of Mines.

‡ Published by permission of the Director, U.S. Bureau of Mines.

About 40 years ago the Tennessee Coal, Iron and Railway Co. attempted to concentrate the Alabama hematite ores by roasting and magnetic separation. This was nobly fostered by Dr. William B. Phillips, who described the work done on these ores in Volume 25 of our TRANSACTIONS. While it was doomed to failure in advance owing to defective methods employed, it was a daring attempt, which cleared the way for those better methods of cooperation which the future surely holds in store for these ores.

The second attempt was made about 30 years ago by Thomas A. Edison, who undertook to concentrate a New Jersey magnetite ore that contained only about 20 per cent metallic iron. Even genius cannot accomplish the impossible, and with the discovery of the rich Mesabi ores about that time, which could be mined cheaply, this enterprise came to an end. Edison had a rather naive indifference to the theoretical side of physical science, but an inspired confidence in the value of new mechanical combinations. His titanic energy created new methods of crushing rock with giant rolls, new methods of handling the rock, as well as several new methods of magnetic separation.

Another attempt was that of the Mesabi Iron Co., which undertook about 10 years ago to concentrate the low-grade magnetite ores of the easterly end of the Mesabi Range. This has been fully and interestingly described by A. B. Parsons in the *Engineering and Mining Journal* of Jan. 26 and Feb. 2, 1924. The deposit contains an almost unlimited tonnage of ore averaging about 30 per cent iron very low in phosphorus but associated with a very hard cherty gangue. Heroic efforts were made to achieve a profit, but the apparatus of the flow sheet did not lend itself to the progressive enrichment of the concentrate that might have lifted it into a new use. All this experience in pioneering on a great scale cannot be lost and the future surely holds out the hope of an eventual success by better technical cooperation.

I have cited these three cases mainly to illustrate the need of intensive cooperation in order to give magnetic separation its rightful place in ore dressing, yet it is also obvious that each of the cooperating means must play its full part. Magnetic separation is itself still at fault. For example, if we crush magnetite successively finer and finer we notice that its coercive force greatly increases. When reduced to 50 to 100 mesh in size, the residual magnetism of each particle exerts a pull upon its adjoining particles, which considerably exceeds its own weight. This causes interlocking and entanglement of the gangue particles, which greatly increase the difficulty of a clean separating action. A simple remedy for this difficulty consists in utilizing a separator that employs centrifugal force to overcome the residual magnetism, or the coercive force of the fine ore particles. If, for example, a 6-in. rotor is revolved at 300 r p m, the centrifugal force develops at its surface:

$$F = \frac{Wv^2}{gr} = 76W$$

This develops a force over seven times the weight of each ore particle to overcome the coercive force. This force can be increased or reduced to adapt it to different ores by varying the speed of the rotor. It should be recognized that while magnetic separation may play an important part in cooperation with the blast furnace, yet this imposes a size limitation upon the ore, which precludes its highest enrichment. The future of any process that depends partly upon cooperation with other methods for its success cannot be forecast with any accuracy. However, any process that is capable of progressive improvement is clearly entitled to a field of increasing usefulness.

E. W. SCHILLING (written discussion).—The authors would again like to call to the attention of the readers the original purpose of the article. As pointed out in some of the discussions, work had been done before on the problem of separating

hematite from its gangue by means of hysteretic repulsion. Definite data were lacking, however, as to how the hematite behaved when certain of the variables were changed. Curves from the data taken by the authors were plotted to show exactly the effect of making certain changes of these variables.

It would seem that the process is ready for commercial development. How soon this will take place will undoubtedly depend upon the supply and demand for iron ore. The authors are gratified by the great amount of interest that has been manifested in this work and hope that it will continue until the process becomes of practical application and value.

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Porosity, Reducibility and Size Preparation of Iron Ores

BY T. L. JOSEPH,* MEMBER A.I.M.E.

(New York Meeting, February, 1936)

BLAST furnaces are most efficient thermally when the CO_2 in the top gas is highest. Oxygen introduced in the air blast is converted to CO in the combustion zones. The extent to which CO, generated in front of the tuyeres, is converted later to CO_2 depends upon the ratio of ore to coke in the charge and the degree to which CO_2 , formed by reduction of iron oxides with CO, reverts to CO by the secondary reaction $\text{C} + \text{CO}_2 = 2\text{CO}$. About 300 to 400 lb. of carbon¹ per ton of pig iron is normally involved in the solution-loss reaction or direct reduction of FeO with carbon, which produces the same over-all results; that is, lower CO_2 in the top gas.

Rich² has recently reported a reduction in fuel consumption at slower rates of blowing on two furnaces in spite of higher heat losses per ton of iron. Lower fuel consumption at slow operating rates was due to more complete reduction of the ore that resulted in higher CO_2 in the top gas and consequently more efficient use of carbon. Kinney³ has reported substantial savings in fuel as a result of crushing and sizing the ore charge. Improvements in practice brought about by sintering magnetite concentrates, flue dust and fine ores have been due to the establishment of conditions favoring more complete reduction of the ore in the upper part of the furnace.

The extent to which oxides and fluctuations in composition in pig iron affect the quality of steel and finished product needs further study. There is evidence that more thorough preheating and reduction of the ore in the upper part of the furnace tend to give a better quality of iron. Bogatzkii⁴ found from laboratory work that the amount of oxygen entering electrolytic iron, melted under various slags, was directly proportional to the concentration of free FeO in the slag and inversely proportional to the basicity of the slag. Herty and Gaines⁵ concluded that the silicate content of open-hearth steel before deoxidation is related to the concentration of silica in the pig-iron charge, indicating that most of the persistent inclusions are silica from the iron. They also found that

Manuscript received at the office of the Institute Nov. 18, 1935. Published by permission of the Director, U.S. Bureau of Mines.

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increases in the silicates in the iron were more pronounced during major variations in the silicon in the iron.

Surveys^{3,6,7} of industrial furnaces made by the Bureau of Mines have demonstrated that notwithstanding advances already made, difficulties

TABLE 1.—*Type, District and Analysis of Ores Investigated*

No	Type	District	Analyses, Per Cent				
			Fe	Mn	SiO ₂	Al ₂ O ₃	Loss on Ignition
1	Hematite	Mesabi	62 6	0 2	6 44	1 34	3 45
2	Hematite	Mesabi	44 7	1 7	32 38	0 96	2 39
3	Hematite	Mesabi	55 1	3 0	8 3	2 90	6 65
4	Limonitic mangiferous	Cuyuna	39 8	8 2	12 8	5 12	15 10
5	Hematite	Mesabi	64 7	0 3	2 64	0 88	3 75
7	Hematite	Mesabi	56 8	1 4	6 42	1 74	8 60
8	Hematite	Cuyuna	60 0	0 2	5 04	5 58	2 06
10	Hematite	Mesabi	60 0	1 9	5 04	3 68	2 76
11	Limonite	Mesabi	59 5	0 3	3 18	1 32	10 13
12	Hematite	Mesabi	61 3	4 2	1 84	1 13	3 70
13	Hematite	Mesabi	56 9	0 3	11 42	1 01	4 20
16	Limonitic mangiferous	Cuyuna	46 0	5 32	6 84	4 64	13 42
17	Limonite	Marquette	51 0	0 3	12 80	0 74	7 70
18	Hematite	Marquette	54 5	0 8	15 04	3 05	1 49
19	Hematite	Western	58 0	0 2	9 98	3 71	2 02
20	Magnetite	Western	51 1	1 0	7 00	2 88	3 33
21	Hematite	Mesabi	48 7	3 0	8 18	8 07	12 04
22	Hematite	Southern	38 2	0 2	9 00	5 25	12 80
23	Hematite	Southern	37 8	0 4	14 37	4 81	12 52
25	Hematite	Western	55 5	0 3	8 36	3 46	4 85
26	Hematite	Cuyuna	54 4	0 3	19 50	1 56	0 48
27	Hematite	Cuyuna	66 4	0 3	4 2	2 14	0 90
32	Hematite	Mesabi	48 0	5 4	6 7	5 22	12 15
33 ^a	Hematite	Southern	36 6	0 6	14 1		18 35
34 ^b	Hematite	Southern	34 8	0 4	20 9		8 65
35	Briquet	Moose Mt.	63 7	0 02	7 36	1 96	
37	Compact limonite	Marquette	56 6	0 13	7 24	2 94	
38	Compact limonite	Marquette	57 0	0 21	5 74	1 72	
39	Compact limonite	Marquette	54 0	0 07	12 02	0 90	
40	Hematite	India	65 7	Nil	0 60	2 70	
41	Hematite	India	63 2	0 07	4 06	2 94	
42	Hematite	India	61 2	Nil	0 42	2 49	

^a 20 8 per cent CaO

^b 10 4 per cent CaO.

inherent in the process leave much to be desired in improving the upper part of blast furnaces from the standpoint of heat interchange and uniformity in gas distribution, temperature and gas composition. All

these factors have an important bearing upon proper preparation of the charge in the shaft, fuel consumption, regularity of operation and uniformity of product. Collateral laboratory studies^{8,9,10} and tests with experimental blast furnaces¹¹⁻¹⁴ have been directed toward studying methods of maintaining more uniform conditions in the shaft.

REDUCIBILITY OF IRON ORES

Differences in the reducibility of iron ores have been recognized by blast-furnace operators and established by laboratory investigation. It has been known that limonites reduce more rapidly than dense hematites and that unaltered magnetites reduce very slowly. It is important, however, to have quantitative information that can be applied by furnace operators in the blending of ores and particularly in determining the size to which coarse, dense ores should be crushed to permit more complete reduction in the upper part of the furnace where low temperatures retard conversion of CO_2 to CO .

Iron Ores Investigated

A wide variety of iron ores, of analyses and origins as given in Table 1, were assembled for study. The names of the ores are not listed because the samples studied may or may not be representative. Ores were selected to cover a wide range in physical properties in the hope that some physical property determinable on a number of bulk samples would give a key to reducibility that could be applied in practice. Ores classed as limonites were characteristically yellow and showed comparatively large losses in weight on ignition. There is, however, no sharp distinction between limonites and hematites. Accordingly, some of the hematites contained limonitic material. Ore 21 is weathered or altered magnetite, and 12 to 20 per cent of ore 25 is also magnetite, the remainder being hematite. Some ores listed as limonitic (for example, ore 11) were of the soft, extremely porous variety, while some of the other limonitic material was more compact, as shown by ores 37, 38 and 39. As pointed out later, the porosity of the ore appears to be more suitable for judging reducibility than a general classification as limonite and hematite.

Physical Properties of Iron Ores

In the upper part of the blast furnace the ore is dried and heated sufficiently to dehydrate limonitic material before significant reduction occurs. Cubical specimens, approximating $\frac{9}{16}$ in. and having a volume of about 3 c.c., were accordingly heated to 500°C . before apparent and true density determinations were made. The size and shape of specimen were selected to simplify preparation of the specimens and to provide

uniform exterior surface conditions for reduction tests. Apparent density determinations were made on the basis of the weight of the cube after heating for 12 hr. at about 450° C., and the volume was determined by the weight of mercury displaced. True density determinations were made by the pycnometer method on minus 100-mesh particles heated to about 500° C. The minus 100-mesh pulps were prepared from the same lumps from which the cubes were made. In true density determinations 10-gram samples were used in 50-c.c. gravity bottles. The percentage of porosity was calculated from the apparent density and true density by the formula:

$$\text{Percentage of porosity} = 100 - \left(\frac{\text{apparent density}}{\text{true density}} \times 100 \right)$$

The data for the various ores are given in Table 2. The heating of ores containing calcium carbonate was adjusted to dehydrate the specimen without calcining the carbonate, because it appears that calcination and reduction of such ore proceed simultaneously in the blast furnace. If completely calcined before reduction, ore high in lime would indicate a higher porosity and higher order of reducibility than could be realized in the blast furnace.

Mercury displacement furnished an accurate method of determining the volume of the cubes that could not be prepared rapidly to precise dimensions. The heterogeneous character of some ores introduced errors in determinations of true density because there was no certainty that the true density of the material in the cube was precisely the same as the remaining part of the lump from which it was made. It was necessary to preserve the form of the cubes, as the main purpose in preparing them was to provide comparable surface conditions during reduction tests.

Certain specimens reduced much more slowly than indicated by their porosities and by the general relation established between porosity and reduction rates of 110 specimens. High true-density values were thought to be the source of error. Five specimens giving such results were reoxidized after the necessary reduction data were obtained. True densities on the reoxidized material were lower than those with the normal procedure. Column 1 in Table 3 gives the porosity as normally determined; column 2, the porosity determined on the reoxidized material; and column 3, the porosity indicated by reduction rates and by the average relation referred to above between porosity and reducibility. The porosity values in column 2 are lower than those normally obtained (column 1) and in closer agreement with the porosities one would expect from reducibility tests (column 3).

Apparent densities ranged from 1.64 for ore 11, a soft porous limonite, to 4.87 for ore 41a, a high-grade dense hematite. True density determina-

TABLE 2.—*Summary of Physical Properties and Reduction Data on Iron Ore*

Ore Specimen	Weight of Cube, Grams	Volume, C.c	Appar-ent Density	True Density	Porosity	Minutes for 90 Per Cent Reduction	Total Water Formed, Grams	H ₂ O per Min per Gram Total H ₂ O Formed*, Mg.
1a	12 1420	2 955	4 11	4 79	14 2	60	3 8394	15 0
b	12 4460	3 056	4 07	4 79	15 0	64	3 8807	14 1
					Av 14 6	62		14 6
2a	12 0977	3 103	3 90	4 30	9 0	72	3 1455	12 5
b	12 8670	3 338	3 85	4 30	10 0	70	3 3130	12 9
c	8 7925	2 844	3 09	4 20	26 2	32 5	2 9237	28 1
					Av 15 1	58 2		17 8
3a	8 4430	2 850	2 96	4 73	37 3	26	2 695	34 61
b	10 4225	3 500	2 98	4 73	37 0	28 5	3 308	31 6
c	9 8462	3 097	3 18	4 73	32 8	35 0	3 297	25 7
					Av 35 7	29 8		30 6
4a	9 7190	3 114	3 12	3 95	21	38	3 049	23 7
b	9 3975	3 004	2 13	3 98	46 0	27 5	0 4667	32 7
c	5 6370	2 766	2 04	3 98	49 0	27 0	0 7162	33 3
					Av 38 7	30 8		29 9
5a	9 2935	3 338	2 78	4 20	33 8	27 0	2 3145	33 3
b	8 5140	3 026	2 81	4 66	39 6	24 0	2 6265	37 5
c	8 5564	3 146	2 72	4 66	41 6	24 5	2 7468	36 8
d	11 7400	3 242	3 62	4 90	26 0	37 5	3 7657	24 0
e	9 7045	3 011	3 22	4 90	34 1	32 5	3 0835	27 7
f	15 2330	3 330	4 57	4 83	5 4	94 0	4 8250	9 6
g	14 1378	3 221	4 39	4 83	9 2	70 5	4 1918	12 8
					Av 27 1	44 3		26 0
7a	7 0110	2 709	2 588	4 67	44 3	22 0	2 2115	40 9
b	8 4170	3 234	2 603	4 35	39 4	29 0	2 4240	31 0
c	8 7127	3 238	2 691	4 35	38 0	30 0	2 4726	30 0
					Av 40 6	27 0		34 0
8a	12 8345	2 990	4 290	4 82	11	59 0	4 3679	15 3
b	12 9387	3 028	4 27	4 82	11	64 0	4 3170	14 1
c	9 7265	2 900	3 35	5 10	34	37 0	3 0363	24 3
d	9 3250	2 989	3 12	5 10	38 7	33 0	2 8482	27 3
					Av 23 7	48 3		20 3
10a	6 0565	3 017	2 01	4 77	57 9	25 0	1 690	36 0
b	6 1885	2 908	2 13	4 77	55 6	26 0	1 8207	34 6
c	5 7090	2 893	1 97	4 77	58 6	20 0	1 647	45 0
					Av 57 4	23 7		38 5
11a	4 876	2 974	1 64	4 86	66 2	19 0	1 636	47 4
b	5 140	3 144	1 64	4 86	66 3	18 0	1 5935	50 0
					Av 66 2	18 5		48 7
12a	11 0355	2 940	3 75	4 57	17 7	58 0	3 5133	15 5
b	9 3120	2 994	3 11	4 57	31 8	35 0	3 0643	25 7
					Av 24 7	46 5		20 6
13a	6 7475	2 654	2 54	4 32	41.	23	1 8950	39 1
b	6 3655	2 658	2 40	4 32	45	21	1 5525	42 8
					Av. 43	22		41 0
16a	9 3370	3 292	2 84	3 74	24	40	2 286	22 5
17a	9 8695	3 465	2 85	3 90	26 8	36	1 5855	25 0
b	12.7133	3 329	3 82	4 52	15 5	60	3 5665	15 0
					Av. 21 2	48		20 0

* Milligrams of H₂O between 0 and 90 per cent reduction per minute per gram of total H₂O formed

TABLE 2.—(Continued)

Ore Specimen	Weight of Cube, Grams	Volume, C c	Appar-ent Density	True Density	Porosity	Minutes for 90 Per Cent Reduction	Total Water Formed, Grams	H ₂ O per Min per Gram Total H ₂ O Formed*, Mg
18a	14.8165	3 200	4 63	5 03	8 0	73 0	3 800	12 3
b	16 2140	3 172	5 12	5 03	0	116 5	5 270	7 7
					Av 4 0	94 8		10 0
19a	12 1085	2 604	4 65	4 98	6 7	75	3 913	12 0
b	10 7765	2 353	4 58	4 98	8 0	58	3 660	15 5
c	13 0680	2 818	4 64	4 92	6 0	60	4 302	15 0
					Av 6 9	64 3		14 1
20a	11 6610	3 035	3 84	3 91	1 82	115 0	2 8245	7 8
b	12 3293	3 116	3 96	4 62	14 40	71 5	3 2339	12 6
					Av. 8 1	93 8		10 2
21a	9 3310	3 030	3 07	4 66	31 5	31 5	2 7436	28 5
b	11 2469	2 989	3 76	4 66	57 0	57 0	2 7029	15 8
c	7 8610	2 836	2 81	4 86	39 5	39 5	2 4607	22 8
d	10 4143	3 222	3 23	4 86	45 0	45 0	3 1014	20 0
e	9 9803	3 128	3 19	4 86	38 5	38 5	3 0073	23 4
f	7 3658	2 535	2 91	4 77	40 0	40 0	2 322	22 2
					Av 28 8	41 9		22 1
22a	10 0365	3 034	3 31	3 69	9 3	65 0	2 1485	13 9
b	10 9757	3 068	3 58	3 69	3 0	100 0	2 5745	9 0
c	10 7320	3 181	3 37	3 69	8 5	71 5	2 3702	12 6
					Av 6 9	78 8		11 8
23a	11 7469	3 287	3 57	3 69	2 2	93		9 7
b	10 0742	2 920	3 45	3 69	6 8	75		12 0
					Av 5 0	84		10 8
25a	11 3625	3 410	3 33	4 48	25 60	39 5	2 8925	22 8
b	12 7720	3 494	3 66	4 17	11 2	51 0	2 9260	17 6
c	10 7493	3 019	3 56	4 17	14 4	52 0	2 9668	17 3
d	10 1843	2 786	3 66	4 17	11 2	64 0	2 7739	14 1
e	11 5520	3 037	3 80	4 17	8 7	58 5	2 8816	15 4
f	10 7292	3 039	3 53	4 55	22 3	34 0	2 9668	26 5
g	11 4427	3 148	3 04	4 55	20 0	44 5	2 9565	20 2
h	8 9205	2 810	3 18	4 55	30 1	28 0	2 5694	32 2
i	10 3145	3 049	3 38	4 55	25 5	35 0	2 9225	25 7
					Av 18 8	45 2		21 3
26a	10 0942	3 149	3 48	4 72	26 5	34 0	2 9315	26 5
b	11 2630	3 013	3 74	4 72	21 0	45 0	3 5525	20 0
					Av 23 7	39 5		23 3
27a	9 5785	3 041	3 15	5 09	37 1	33 0	3 0895	27 3
b	9 5789	3 000	3 19	5 06	36 9	36 5	3 1782	24 7
c	10 8185	3 059	3 54	5 00	29 4	46 0	3 547	19 6
d	11 2543	3 078	3 66	5 00	27 0	46 0	3 6837	19 6
e	8 8750	2 745	3 23	5 00	35 5	37 5	2 966	24 0
f	11 6800	3 110	3 76	5 00	26 0	46 0	3 895	19 6
					Av 31 0	40 8		22 0
31a	15 1412	3 153	4 80	4 73	4 7	53 0	5 060	17 0
b	13 2544	2 942	4 51	4 73	4 7	58 0	4 282	15 5
c	11 4085	3 103	3 67	4 73	22 2	36 5	3 8426	24 7
d	14 2378	3 159	4 51	4 73	4 7	50 5	4 7578	17 8
					Av 7 9	49 5		18 8
32a	6 1255	3 185	2 11	4 68	54 8	20 0	1 672	45 0
b	6 109	2 900	2 11	4 68	55 0	22 5	1 724	40 0
					Av 54 9	21 3		42 5

* Milligrams of H₂O between 0 and 90 per cent reduction per minute per gram of total H₂O formed.

TABLE 2.—(Continued)

Ore Specimen	Weight of Cube, Grams	Volume, C.c.	Apparent Density	True Density	Porosity	Minutes for 90 Per Cent Reduction	Total Water Formed, Grams	H ₂ O per Min. per Gram Total H ₂ O Formed*, Mg
33a	11 0813	3 096	3 58	3 64	1.8	115	2 4605	7 8
b	11.1436	3 072	3.63	3.64	0.5	115.	2 5113	7.8
					Av. 1 2	115		7 8
34a	9 4120	2 827	3 33	3 63	8 2	70	1 9247	12 9
b	10 3610	3 031	3.42	3 63	5 8	73 5	2 3524	12 2
					Av. 7 0	71 7		12.6
35a	9 8470	3 054	3 22	4 79	32 7	34 0	3 0078	26 5
b	10 084	3 171	3 18	4 52	29.8	33 0	2 9357	27 3
					Av. 31 2	33 5		26 9
37a	6 635	2 874	2 31	4 11	43 8	30	1 8565	30 0
b	11 1110	3 155	3 52	4 27	17 5	44 5	3 6681	20 2
c	12 3385	3 259	3 79	4 27	11 4	60 0	4 0051	15 0
d	11 6405	3 286	3 64	4 27	17 1	46 0	3 8885	19 6
e	7 0013	3 201	2.19	4 27	48 8	27 0	1 7021	33 3
					Av. 27 7	41 5		23 6
38a	11 4220	3 2548	3 51	4 11	14 6	45 0	2 9005	20 0
b	8 3286	3 121	2 67	4 19	36 2	25 5	2 6328	35 3
c	9 0250	3 291	2 74	4 19	34 4	31 0	1 7917	29 0
					Av. 28 4	33 8		28 2
39a	5 9915	2 5103	2 39	3 99	40 1	28 0	1 6321	32 2
b	9 6905	3 274	2 96	3 81	22 4	51 0	1 8687	17 7
c	8 7012	3 038	2 86	3 81	24 8	29 5	2 7493	30 5
d	10 0005	3 103	3 22	3 81	15 3	44 0	3 0414	20 5
					Av. 25 7	38 1		25 0
40a	11 9580	3 0150	3 97	4 47	11.0	66 5	3 9400	13 5
b	11 8230	2 8943	4 09	4 47	7 0	64 0	3 8640	14 1
c	6 7775	3 4860	1 94	3 86	49 6	21 5	1 0227	41 8
d	7 7275	3 200	2 42	3 86	37 3	32 0	1 3560	28 1
					Av. 26 7	46 0		24 4
41a	11 5720	2 8943	4 09	4 59	12 0	65 0	3 507	13 9
b	16 5869	3 406	4 87	5 04	3 2	106 0	5 422	8 5
c	15 9257	3 384	4 71	5 04	6 4	83 0	5 174	10 8
					Av. 7.2	84 7		11 1
42a	9 6150	3 639	3 04	4 67	35 0	28 5	3 0858	31 6
b	8 7265	2 868	3 04	4 67	35 0	34 0	2 7970	26 5
c	9 1230	2 892	3 16	4 67	32.5	35 0	2 8900	25 7
d	9 1310	3 215	2 84	4 83	41 2	28 0	3 0032	32 2
e	13 3700	3 224	4.15	4 83	14 0	55 0	4 4828	16 4
					Av. 31 5	36 1		26 6

* Milligrams of H₂O between 0 and 90 per cent reduction per minute per gram of total H₂O formed.

tions, governed largely by the iron content of the specimens, ranged from about 3.6 for Alabama ores 22, 23, 33 and 34 to slightly more than 5.0 for some of the specimens high in iron. The percentage of porosity ranged from about zero for hard, dense hematites to about 66 for ore 11.

Reduction Tests

The cubical specimens used in porosity determinations were reduced in a stream of hydrogen at 800° C. The apparatus used is essentially the

same as that shown diagrammatically in Fig. 1. A quartz tube containing platinized asbestos was substituted for the alloy steel tube indicated by *B*. Another change was made by inserting a pad of nichrome wire screen in the end of the reduction furnace through which the purified hydrogen entered. This pad, which conformed in shape to refractory tube *E*, aided in bringing the hydrogen up to the temperature of the furnace before it came in contact with the ore specimen.

TABLE 3.—Data Indicating True Density Determinations as a Probable Source of Error in Determining Porosity of Heterogeneous Iron Ores

Specimen	Porosity	Porosity	Porosity
	(1)	(2)	(3)
21a	42.0	36.0	25 0
b	33 4	25 4	20 0
c	34 2	28.0	26 0
d	33 9	21 5	33 0
e	19 2	14 2	13 5

Dry, dehydrated ore specimens were placed in one end of a nichrome-wire-screen boat and either inserted quickly into a cold furnace or moved slowly into a hot furnace until the specimen was adjacent to the thermocouple. Nitrogen was passed through the system until the specimen came up to temperature. Normally 20 min. was allowed after the thermo-

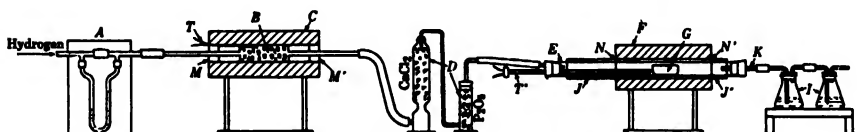


FIG. 1 —REDUCTION APPARATUS

A Flowmeter. E Refractory tube. J-J' Asbestos paper wrappings.
 B Alloy steel tube. F Electric furnace. K Brass tube.
 C Electric furnace. G Nichrome wire screen boat. M-M'-N-N' Asbestos cement.
 D Drying bottles. I Absorption flasks. T-T' Thermocouples.

couple registered 800° C. before the nitrogen was cut off and hydrogen introduced. About 1 min. was required to establish the designated rate of flow of hydrogen. Zero time for a reduction test was taken as the instant when hydrogen was introduced. Care was taken, particularly during the early stages of reduction, to hold the rate of flow of hydrogen at 600 c.c. per minute to maintain an excess of hydrogen. A temperature of 800° C. was selected to avoid reduction of MnO and silica and yet provide as rapid a reaction rate as possible to save time. The outlet end of the reduction furnace was heated slightly with a low flame to prevent condensation of water.

can be determined. To express reducibility by a single numerical value, the time required for 90 per cent reduction was taken as an index of reducibility. This degree of reduction was selected rather than 100 per cent because in some cases the rate of reduction decreased sharply beyond about 90 per cent reduction. There was considerable uncertainty as to the exact moment for 100 per cent reduction, but by plotting the degree of reduction against time, as shown in Fig. 2, the time for 90 per cent reduction shown by the vertical lines was established within $\frac{1}{2}$ min. The time required for 95 per cent reduction could be used, but in ores reduced rapidly under the conditions maintained 90 per cent reduction appeared to offer a better basis of comparison.

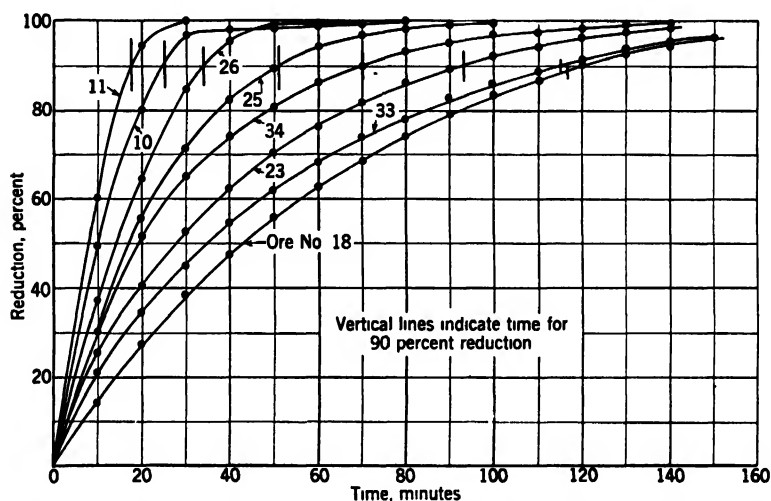


FIG. 2—TYPICAL CURVES SHOWING PERCENTAGE OF REDUCTION WITH TIME

RELATION BETWEEN POROSITY AND RELATIVE REDUCIBILITY OF IRON ORES

The reduction of iron oxides by CO or hydrogen is a heterogeneous reaction between a gas phase and a solid phase. Such reactions proceed at rates proportional to the solid surface exposed when other factors are constant. Fine ores present a large surface, but mechanical difficulties limit the quantity of reducing gases that can be applied to the surface of fine particles in the blast-furnace and similar processes that involve a countercurrent circulation of gases and solids. The relative reducibility of fine ore is not important. Such material should be converted into a porous agglomerate for effective mass reduction. The Bureau of Mines, accordingly, has recommended sintering or other methods of agglomeration for preparing fine ores for use in the blast furnace¹⁰. Sintering of

fines and segregation of plus $\frac{3}{8}$ -in. particles into several sizes provide conditions favorable to mass reduction.

The present study shows the importance of porosity in reduction. It is intended primarily however for use in connection with hard, dense, coarse ores. To establish the relative reducibility of fine ore from the standpoint of its use in a blast furnace would involve consideration of its screen analysis and difficulties inherent in maintaining a uniformly permeable bed or column of stock.

With certain Lake Superior ores, particularly with the Alabama, Wyoming, New Mexico and Utah ores, it is difficult to determine how fine the ore should be crushed to permit reduction of the central area of coarse lumps. The present study was projected primarily to furnish information on this problem.

Table 2 shows an inverse relation between the time required for 90 per cent reduction and the percentage of porosity. This relation is shown for 110 ore specimens and averaged for 33 ores in Fig. 3. There is some scattering of points due to errors in porosity data and to variations in the character of the porosity and in the amount of checking or cracking that occurred during reduction. The difficulty in obtaining accurate data on the true density and the subsequent introduction of errors in porosity calculations were discussed earlier in this paper, under the heading of Physical Properties of Iron Ores.

Permeability measurements showing the effect of differences in the character of the porosity probably would show a closer relation to reduction rates than

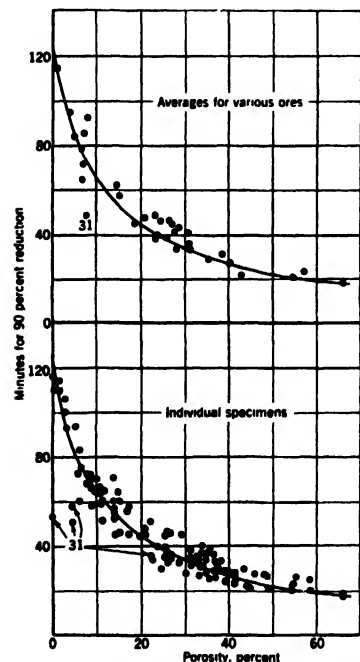


FIG. 3.—RELATION BETWEEN POROSITY AND TIME FOR 90 PER CENT REDUCTION OF IRON ORES.

total porosity values, which do not indicate whether the pores are large or small or interconnected. Permeability studies were abandoned because it would be tedious to make the observations necessary to provide representative data that could be applied in practice.

In many specimens checking or cracking occurred during reduction. Probably it occurred during the later stages of reduction and for this reason did not mask the effect of porosity. Specimens of ore 31 cracked and split into several pieces. Therefore these specimens show an abnormally short time for 90 per cent reduction, although their porosities were low.

RELATION BETWEEN POROSITY AND RECIPROCAL OF TIME REQUIRED FOR 90 PER CENT REDUCTION

Average data from the curves in Fig. 3 are given in Table 5. The third column of this table gives the reciprocal of the time required for 90 per cent reduction times 10^3 . If the reciprocal of the time required for 90 per cent reduction is plotted against the percentage of porosity, a straight-line relationship (Fig. 4) is obtained. Ores approaching zero porosity have a reducibility of 8 compared to one of about 57 for ores with a porosity of 66 per cent.

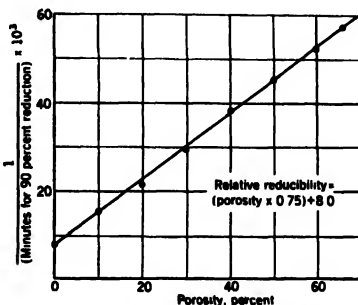


FIG. 4—RELATION BETWEEN POROSITY AND RELATIVE REDUCIBILITY OF IRON ORE.

Reduction of hard, dense ore is confined to the exterior surface in the early stages. As reduction progresses toward the center of the piece the porous exterior of sponge iron provides openings for diffusion of reducing gases inward and of the product of reduction outward.

TABLE 5.—Average Data Showing Relation between Reciprocal of Time for 90 Per Cent Reduction and Porosity

Porosity	Minutes for 90 Per Cent Reduction	$\frac{1}{(\text{Minutes for 90 Per Cent Reduction})} \times 10^3$
0	125*	8 0
10	65	15 4
20	45	22 2
30	34	29 4
40	26	38 5
50	22	45 5
60	19	52 6
66	17 5	57 1

* Points taken from Fig 3.

RELATION BETWEEN RATE OF WATER FORMATION BY HYDROGEN REDUCTION AND POROSITY OF IRON ORE

The rate at which water is formed by reduction with hydrogen is influenced by the amount of iron oxides in the sample as well as by the physical character of the samples. Other things being equal, the rate of water formation will increase directly with the amount of iron oxides in the sample. This mass action can be compensated for by expressing rates of reduction in terms of the water formed per minute per gram of total

water formed. The last column in Table 2 gives the milligrams of water formed per minute between 0 and 90 per cent reduction per gram of total water formed. In detail this expression is as follows:

$$\frac{\text{Grams total water formed} \times 0.9 \times 1000}{\text{Minutes for 90 per cent reduction} \times \text{total water formed}} = \frac{900}{\text{Minutes for 90 per cent reduction}}$$

Rates of reduction expressed in this way are based essentially upon the length of time required for 90 per cent reduction. As shown in Fig. 5, the rate of water formation varied directly with the porosity. In dense ores with a porosity of 1 or 2 per cent, water was formed at a rate of

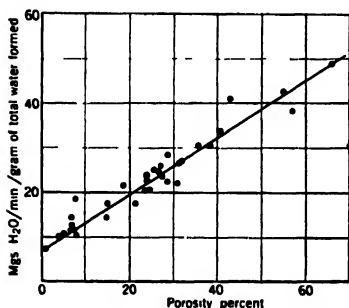


FIG. 5.—RELATION BETWEEN POROSITY OF IRON ORES AND RATE OF WATER FORMED BY HYDROGEN REDUCTION.

about 7 mg. of water per minute per gram of total water formed compared with a similar rate of 49 for an ore with a porosity of 66. The slow rate of 7 mg. per minute results when reduction is first confined to the exterior and reducing gases finally reach the center of the particle because of the porous exterior resulting from reduction. Reduction in such cases is probably confined to a narrow zone in which gradations from metallic iron to hematite occur. The more porous the ore the more readily gases diffuse in and out of it. In such ores a gradation from metallic iron on the surface through solid solutions of FeO and magnetite toward the center probably is rapidly established so that oxygen is removed from iron by reduction across a much wider zone.

APPLICATION OF RELATION BETWEEN POROSITY AND RELATIVE REDUCIBILITY

The relative reducibility of ores can be established directly by reduction tests such as those previously discussed. For ores of uniform structure satisfactory results could be obtained, but for small samples some doubt would remain as to whether the results were representative.

It appears advisable to determine the porosity of a number of bulk samples and from a representative porosity value thus obtained to determine the relative reducibility based on the general relation between porosity and reducibility. As a check upon the possibilities of such procedure, five 50-lb. samples were obtained of ore 25, which is of particular interest because crushing to 2 in. and sizing have given satisfactory furnace practice on this particular ore. Moreover, the Bureau of Mines

found from surveys of a furnace operating on this ore that reduction was 96.6 per cent complete at the top of the bosh. (See p. 83 of ref. 3.)

About 10 lb. from each of the five 50-lb. samples was placed in a sheet-iron box, 6 by 9 by 3½ in., then heated in an electric muffle furnace for 12 hr. at about 450° C. The loss in weight of about 3 per cent provided a means of reducing the weight of the entire sample to a dehydrated basis. If facilities were available, the entire sample could be heated to a dehydrating temperature. The remainder of each 50-lb. sample was next weighed in the "as-received" condition and the factor applied for converting it to a dehydrated basis. Ore lumps were approximately 2 in. in diameter.

The apparent specific gravity of each of the five 50-lb. samples was next determined by the method used in determining the apparent specific gravity of lump coke¹⁵. The volume of the ore was obtained by determining the weight of water displaced and by adding to this the weight of the water absorbed by the ore. The apparent specific gravity of the dehydrated ore equals $\frac{A}{B + (C - D)}$, where A is the equivalent weight of dehydrated ore, B the weight of water displaced, C the weight of wet ore, and D the weight of ore before it was immersed in water.

A wire-screen cage 10 by 10 by 10-in., with ½-in. openings, was satisfactory for immersing the ore in water. A tank, 14 by 14 by 14 in., made of 18-gage galvanized sheet iron with a short ½-in. pipe nipple welded 1½ in. from top, provided a suitable container for the water. The results of apparent specific-gravity determinations are given in Table 6.

TABLE 6.—*Apparent Specific Gravity of Bulk Samples of Iron Ore*

Sample No.	Equivalent Weight of Dehydrated Ore, Lb.	Natural Basis, Lb.	Wet Ore, Lb.	Water Displaced, Lb.	Apparent Gravity	True Gravity	Porosity, Per Cent
1	47 23	49 17	50 74	11 68	3 56	4.56	21 88
2	48 06	49 27	50 88	12 12	3 51	4 50	21 90
3	47 62	49 12	51 02	12 42	3 32	4 46	25 49
4	48 06	49 60	51 42	12 46	3 37	4 53	25 57
5	37 07	38 18	39.40	9 60	3 43	4 51	24 01
Average					3 44	4 51	23 77

$$\text{Apparent specific gravity} = \frac{\text{Column 1}}{\text{Column 4} + (\text{column 3} - \text{column 2})}$$

True density determinations were made on minus 100-mesh pulps prepared from each of the five samples. These minus 100-mesh samples were heated about 12 hr. at 450° C. Ten-gram samples were weighed in the dehydrated condition for true gravity determinations by water

displacement in 50-c.c. gravity bottles. The usual precautions were taken of using freshly boiled water and boiling the sample to eliminate air.

COMPARISON OF APPARENT DENSITY, TRUE DENSITY AND
POROSITY DETERMINATIONS ON 10-GRAM AND 50-LB.
SAMPLES OF ORE 25

Table 2 gives the apparent densities, true densities, and porosities of nine small samples of ore 25. Apparent densities ranged from 3.18 to 3.80, averaging 3.53, while similar determinations on 50-lb. samples ranged from 3.32 to 3.56, averaging 3.44. True densities ranged from 4.17 to 4.55 on the small samples compared with 4.46 to 4.56 on the 50-lb. samples. Specimens 25*b*, *c*, *d* and *e* were selected to represent the dense phase of this ore. From the appearance of the sample the porous phase, represented by specimens 25*a*, *f*, *g*, *h* and *i*, predominated over the dense phase in the ratio of about 3 to 1. This accounts for the lower average porosity of the small samples (18.8) compared to the bulk samples (23.77). On the basis of a 3 to 1 ratio of porous to dense lumps the porosity of the small samples would be 23.9 compared to 23.77 for the bulk samples.

In the selection of small samples from all ores for reduction tests, an effort was made to obtain the extremes in the ore structure. Consequently the rate of reduction of specimens from the same ore varied widely. As a rule large differences in porosity were reflected in the rate at which the specimen reduced. Such variations show clearly the need for either a large number of more accurate tests on small samples or fewer, less accurate tests on large samples to obtain representative data. Reduction tests cannot be made readily on large samples, but representative porosity data are sufficient to appraise the relative reducibility of an ore and to afford a basis for determining the size to which it should be crushed.

POROSITY AND SIZE OF ORE LUMPS FOR BLAST-FURNACE USE

If large lumps of hard, dense ores are charged into blast furnaces, they will reach the top of the bosh and the fusion zone with unreduced centers. The size of such ores should be reduced according to the porosity, which has been shown to bear a direct relation to the time required for reduction. Finer crushing has improved furnace practice on Alabama ores and Utah ores. Some criteria for determining the size to which an ore should be crushed should stimulate further progress in this direction.

Instead of laboratory tests being used to determine the time required for reducing ores under blast-furnace conditions, ore 25 (smelted at Provo, Utah) is taken as a basis for relating porosity, reducibility and size of crushing. The porosity of this ore averaged about 24 per cent,

which would correspond to 40 min. for 90 per cent reduction, according to Fig. 3. Ores ranging from 0 to 10 per cent porosity and averaging 5 per cent, according to Fig. 3, would require 81 min. to reach 90 per cent reduction. As 2 in. has proved satisfactory in practice for the Utah ore it appears that ores ranging from 0 to 10 per cent porosity should be crushed to 1 in. The size of the ore should vary inversely with the time required for reduction ($40:81::X:2$, or $X = 1$), that is, ore requiring twice as long as the Utah ore for 90 per cent reduction should be crushed to one-half the size. Similarly, ores ranging from 10 to 20 per cent porosity required about 53 min. for 90 per cent reduction, compared to 40 min. for the Utah ore. Such ore should be crushed to $1\frac{1}{2}$ in. ($40:53 \times 2 = 1.45$). Other data obtained similarly are given in Table 7.

The size to which ores should be crushed can also be determined from the relation between porosity and reducibility expressed as the reciprocal of the time required for 90 per cent reduction. (See Fig. 4 and Table 5.) Ores ranging from 0 to 10 per cent porosity with an average of 5 per cent have a relative reducibility of 12, compared to a reducibility index of 26 for the Utah ore having a porosity of 24. (See Fig. 4.) As 2-in. pieces of the Utah ore have reduced satisfactorily in practice, an ore with a reducibility index of 12 should be crushed to about 1-in. pieces ($12:25::X:2$, or $X = 0.92$). As the porosity and relative reducibility increase, the size of the ore can be increased. According to Fig. 4, ore with a porosity of 35 will have a relative reducibility of about 34 and

TABLE 7.—*Relation between Porosity, Relative Reducibility and Size of Iron Ore for Blast-furnace Use*

Range of Porosity	Minutes for 90 Per Cent Reduction (Average)	$\frac{1}{(\text{Minutes for 90 Per Cent Reduction})} \times 10^3$	Maximum Ore Size, ^a In.	Maximum Ore Size, ^b In.
		(average)		
	(1)	(2)	(3)	(4)
5 to 10	81	12	1 0	1 0
10 to 20	53	19 0	1 5	1.5
24 (base ore)	40	25 0	2 0	2 0
20 to 30	39	26 0	2 0	2 0
30 to 40	30	33 0	2 7	2 6
40 to 50	24	42 0	3 3	3 3
50 to 60	21	48 0	3 8	3 8

^a Maximum size of ore $X = X:2 \text{ in. (base ore)} :: 40: \text{minutes for 90 per cent reduction}$
 $\text{reduction} = \frac{80}{\text{minutes for 90 per cent reduction}}$

^b Maximum size of ore $X = X:2 \text{ in.} :: \frac{1}{\text{minutes for 90 per cent reduction}} \times 10^3$
 $25 \text{ (base ore)} = \frac{2 \text{ in.} \times (\text{column 2})}{25}$

should therefore be crushed to about 2.6 in. ($3\frac{1}{2} \times 2 = 2.6$). Similar results are given in the last column of Table 7.

In the application of the above data, the character of the ore, particularly the way it breaks on crushing, should be considered. Laminated ores that tend to break in flat, elongated pieces would not require such fine crushing as ores that tend to break into pieces more spherical in shape. Such ore should be crushed according to its width. The amount of fines produced and the tendency of the ore to break up under mechanical action should also be considered. Operators using coarse ores or burdens containing substantial amounts of coarse ores can obtain satisfactory indications from porosity measurements as to whether or not particular ores should be crushed finer and, if so, how much finer. Alabama ores 22, 23, 33 and 34 fall in the range of 0 to 10 per cent porosity. (See Table 2.) According to Table 7 and Fig. 6 such ore should be crushed to minus 1 in. Crockard recently reported that crushing hard Alabama ores to 1 in. has greatly improved practice¹⁶. He also stated that by crushing the ore to $\frac{3}{4}$ in. it is possible to use as much as

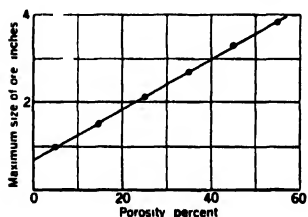


FIG. 6—RELATION BETWEEN POROSITY OF IRON ORE AND MAXIMUM SIZE FOR BLAST-FURNACE USE

25 per cent of an ore that is difficult to reduce and contains more silica than lime. The high-lime Alabama ores, according to practice, are easier to reduce than those containing more silica than lime. This difference was not shown by the laboratory tests and is attributed to the retarding action of the lime in the formation of iron silicate under actual furnace conditions. These practical results, reported by Crockard, justify the position of the low part of the curve in Fig. 6, which indicates that ores approaching zero porosity should be crushed as small as 0.75 inch.

REDUCIBILITY OF ALTERED AND UNALTERED MAGNETITES

As eastern magnetites are largely concentrated and sintered, the reducibility of the crude ore assumes less importance. Preliminary reduction tests on crude, unaltered magnetite indicated slow reduction rates, 380 min. being required for 90 per cent reduction compared to 40 min. on Desert Mound ore from Utah. According to Ramsay¹⁷, the iron in the Utah ore is principally hematite but contains 12 to 20 per cent of magnetite. It seems therefore that weathered or altered magnetites reduce much more rapidly than the unaltered type in New York and New Jersey.

Ore 20, a weathered magnetite from New Mexico, reduced slowly but much more rapidly than the unaltered New Jersey magnetite used in a few reduction tests. The data previously presented relating porosity,

reducibility and size for blast-furnace use do not apply to unaltered magnetites but appear to apply to weathered magnetites. Reduction may be slow owing to the presence of iron silicates or to the compact structure of the magnetite grain or crystal, or to both.

On the basis of 380 min. for 90 per cent reduction of unaltered magnetite compared to 40 min. for the Utah ore, unaltered magnetites should be crushed to $\frac{40}{380} \times 2 = 0.21$ inch.

SUMMARY

Judicious crushing of dense iron ores to a size that will permit more complete reduction in the upper shaft of the blast furnace has resulted in substantial savings in fuel. Fuel requirements per ton of iron on furnaces operating on reduced air blast also have shown clearly the desirability of more complete reduction and preparation of the charge in the upper part of the furnace.

Specimens of iron ores varying widely in porosity were reduced with hydrogen under a set of prescribed conditions. The reducibility, expressed as the reciprocal of the time required for 90 per cent reduction, varied directly with the porosity. The relation developed indicated the degree of crushing for ores within certain ranges of porosity.

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DISCUSSION

(William A. Haven presiding)

C. E. WILLIAMS,* Columbus, Ohio.—In general, I feel that these meetings are very helpful. They are the beginning of a better understanding of the metallurgy of blast-furnace practice and of pig iron, which is very much needed and is going to make it possible to pass on to the practical operating people in increasing degree, the results of technical investigations such as are exemplified by Mr. Joseph's work.

I believe that the facts Mr. Joseph has shown are facts that operators appreciate. If the operators had the means of putting down their information in factual statements such as this, they would show the same thing. But the advantage of having such an investigation as Mr. Joseph has made is that it shows definitely the various factors relating to such questions as the reducibility of ores. In other words, such work serves to take out the mystery and to put the situation into very definite terms. Such work as this offers a means for the more scientific operation of blast furnaces about which more and more is becoming known all the time.

W. A. HAVEN,† Cleveland, Ohio.—For some time past, following Mr. Joseph's original paper on this subject, we have been using in a practical way his method to forecast the smelting requirements of different ores which had never previously been used. We have been obliged to send our samples to Mr. Joseph at Minneapolis and he has, I believe, applied a reducibility test to them. I am interested to know whether this testing is going to take the form of testing for porosity or whether it is going to be this direct reducibility test upon which your whole subject is set up.

T. L. JOSEPH.—I think it would always be desirable to make a few reducibility tests, but the difficulty, as I say, in making a reducibility test is that the ore is heterogeneous. Nevertheless, it would be desirable to make a few such tests to see that the behavior was normal, that you did get the normal relation between reducibility and porosity. For hematite ores and limonite ores, I believe that the relation holds definitely enough so that the porosity will give a pretty fair indication of reducibility.

W. A. HAVEN.—What about the porosity test? Which is easier?

T. L. JOSEPH.—The porosity test could be made by taking, say, a 50-lb. sample and getting its weight after dehydration, submerging it in water and getting the weight of the water displaced, which gives the volume of the ore particles. Knowing the weight of the sample and the volume of the ore from the water displaced, you have data for determining its apparent density. It is necessary to grind down a sample as

* Director, Battelle Memorial Institute.

† Vice President, Arthur G. McKee & Co.

for a laboratory sample and determine the true density. From the apparent density and the true density the porosity can be calculated. It is a very simple procedure and any plant chemist could make such a test.

W. A. HAVEN.—It is simple if water permeability is equivalent to porosity as far as gases are concerned. Is that your theorem?

T. L. JOSEPH.—In this case I took five 50-lb. samples of the ore and determined the porosity on these bulk samples, ranging from $1\frac{1}{2}$ in. up to 2 in. I also prepared 10 cubes of the same ore. The determination of porosity on the small cubes was done very carefully, on the bulk samples less carefully, and they checked reasonably well. So that I believe that the porosity of bulk samples can be determined with reasonable accuracy.

W. A. HAVEN.—Which is more easily accomplished, the porosity test or the reducibility test?

T. L. JOSEPH.—The porosity test is much simpler.

R. S. DEAN,* Washington, D. C.—As I understand it, the author assumes that no water goes into that ore. In other words he is determining apparent density?

T. L. JOSEPH.—The sample is immersed in water to obtain the volume of the particles of ore, not the porosity directly. When the sample is immersed in water it is possible to get the dry weight and the wet weight of the ore. A certain amount of water is absorbed by the ore. The weight of the water absorbed is added to the weight of the water displaced by the ore. The difference between the weight of the wet ore and the dry ore is added to the weight of the water displaced to obtain the volume of the ore particles.

R. S. DEAN.—Then you correct that for the wet and the dry samples?

T. L. JOSEPH.—Yes, these details are all outlined in the paper. I wanted to get along without discussing them here to save time. It is fairly simple if it is thought out. It is the same principle as is used in determining the porosity of bulk coke.

C. HART, Chester, Pa.—What effect have the other elements that exist in iron ores, especially the odds and ends in the way of compounds of iron? Also, how does the test apply to specular ore and to a spathic ore? Which would have a high sulfur content?

T. L. JOSEPH.—As to the other ingredients in the ore, I think that iron silicate would probably disturb this relation materially. I think that material like specular hematite would follow the general relation between porosity and reducibility, because I did, after all, have 32 ores and I covered a wide variety of material.

With regard to ore containing calcium carbonate, the situation is a little more complicated. Some of the southern ores, for example, are of the siliceous type, with an excess of silicon over lime. They require limestone to flux the silica. Then there are the self-fluxing ores. I had four southern ores in this group and they fit the relation between porosity and reducibility. The samples of those ores were not heated before reduction at sufficiently high temperatures to calcine the lime. The temperature was about 450° C. in all cases, so as to drive off all the water but not calcine the lime carbonate present.

In practice, the high-lime ores rust more rapidly, at least they perform better in the furnace than the siliceous ores, yet on these tests in which the sample has not been heated up to calcination that difference is not shown up by the laboratory test.

* Metallurgical Division, U. S. Bureau of Mines.

The reason I did not calcine the sample was that I was not sure whether calcination precedes reduction. I think they go on simultaneously. I still think that the benefit of the lime-bearing ore is due to the self-fluxing action that prevents the formation of iron silicate. As the ore moves down in the furnace there is partial reduction. Iron oxide and silica are closely associated. If the lime is not there ferrous silicate is formed, which is not reduced as readily as if there is sufficient lime to flux the silica and leave the iron oxide more or less free for reduction.

C. HART.—In regard to the high-lime ores, are you not doing the same thing as burning limestone? When limestones are burned to lime, they do not crack up as badly as limonite ore does because there is lump lime. But that lime is so full of holes where the carbon dioxide came out that the ore is in exactly the same condition, and it is a matter of offering surface to the gases.

T. L. JOSEPH.—That is very true, but calcination requires a fairly high temperature.

C. HART.—About 1000° C.

T. L. JOSEPH.—Which precedes? Do you calcine the sample before it is reduced? They go on simultaneously and it is rather hard to determine whether the sample should be completely calcined or not. If I had taken these southern ores with high lime content and calcined the sample I would have gotten a much more rapid rate of reduction because, as you say, they would have been more porous, and I could have determined the porosity and they would have fitted on the curve.

C. HART.—That is really what you are after.

T. L. JOSEPH.—I do not think so. In the blast furnace calcination and reduction go on simultaneously. All the lime carbonate is not calcined before the sample is reduced, because the processes go on together. Water of hydration is practically all driven off before substantial amounts of reduction are obtained.

C. HART.—The ore containing lime gives up its carbon dioxide at practically the same temperature as limestone does, does it not? That is about 30 ft down in the furnace.

T. L. JOSEPH.—Yes, probably they go on simultaneously. But the reason I have some confidence in the method is that it works out very clearly that the southern ore should be crushed to about an inch, according to this relation. Mr. Crockard can tell us something about their practice in the South about crushing ores.

F. H. CROCKARD,* Birmingham, Ala.—When I reported last October,† our practice was to crush all ores through a crusher set at one inch, which did greatly improve our practice.

Our company uses two of the hard ores. I believe they were No. 33 and No. 34 on that chart. The ore with the lime, more than the silica, handles much better in the furnace than the other ore. These two ores are very different in physical appearances. From its appearance, I believe the ore with the higher lime content is much more heterogeneous than the other. There are streaks of white in it, which sometimes must be lime and at other times I believe are probably silica. I never ran an analysis on these ores.

We have changed our practice in the last few months. Our present practice calls for the crusher to be set at $\frac{5}{8}$ in. We then screen the ore over two screens. We

* Metallurgist, Republic Steel Corporation.

† See page 36, this volume.

have one at 1 in., and the plus 1 in. we call the coarse ore, which, of course, is really a very well prepared ore. The bottom screen is $\frac{1}{8}$ in. Therefore, we have two sizes plus 1 in. The second size is minus 1 in. and plus $\frac{1}{8}$ in., and there is the very fine ore through $\frac{1}{8}$ in. We use the two coarser sizes in the furnace, charged separately. The fine ore is being put in stock and we intend to sinter our finer ores. The sintering plant is under construction and probably we will have an interesting report to make on that in a short while.

The ore with the lower amount of lime, which is far from being self-fluxing, does have to be crushed to a very small size in order to be used satisfactorily. We hope some day to be able just to crush it very fine and sinter it all. There is no doubt that finer crushing of the ore is a great help on the dense southern ores.

Mr. Joseph's paper bears out the general idea very well—that 1 in. seems to be the proper size for southern ores. Having gone to smaller sizes and charging separately, I really cannot see much more benefit than we obtained by simply crushing everything down to about an inch and charging it in, except the fact that since we have started taking out the minus $\frac{1}{8}$ in. we have reduced the flue dust. It is apparent that 1 in. is probably the proper size for the southern hard ores, especially the self-fluxing ores. Those that are less than self-fluxing are greatly improved by proper crushing but they still offer further problems, as Mr. Joseph suggested. That is probably due to the early formation of the iron silicate.

W. E. BREWSTER,* South Chicago, Ill.—I do not believe there is any more pertinent subject before blast-furnace men today than the sizing of the materials. I say "materials" because it is just as important to have the other materials in the blast furnace sized as it is to have the ore sized. I am very familiar with the project out in Provo, Utah, which might have been an almost impossible operation but for the sizing of the ores.

I have been much interested in the talk of limonite. The general conception is that the limonitic ore is an asset to a blast furnace. That, I think, is true of all the old-range ores, at least all of those that I am familiar with.

I am going to ask Mr. Joseph if he is willing to say something about the character of the Mesabi limonites, or Mesabi ores that border on the limonitic structure, in the vicinity of Chisholm. The particular ore that I have in mind is a very wet ore, about 18 or 20 per cent of free moisture and about 10 per cent of combined moisture. With that particular ore the characteristic spoken of before, that of being easily reduced, may be true. But before it gets as far as that it goes out of the furnace. In other words, it has a tendency to swell with the application of heat, and is blown out of the furnace in the form of flue dust.

Mr. Joseph can correct me if I am wrong, but we spent about three years finding this out and proving it. Now we are sintering that particular ore with very good results. Nevertheless, this particular ore charged into the furnace seemed to exhibit a tendency to swell up and pop like popcorn. The minute we put that ore on the furnace clouds of red flue dust began to float away in the atmosphere.

T. L. JOSEPH—I think we had some of the ore that you speak of. First I want to point out that there are certain ores that offer mechanical trouble in charging. I don't know in this case whether there was a tendency on the part of the ore to stick on the bell or not.

W. E. BREWSTER—It stands straight up.

* Superintendent of Blast Furnace Dept., Wisconsin Steel Works, International Harvester Co.

T. L. JOSEPH.—Well, if an ore sticks on the bell and upsets the distribution, you are in trouble and there is no way out. Gas distribution is upset and channeling started and a lot of dust is produced. That is an indirect effect. But that ore will do that when it is wet, because of a certain amount of stickiness or plasticity. Those things cannot be covered completely in such a situation as this.

I agree with the practical man—in the last analysis, you have to try the ore in the furnace. But, we do need some of these principles as a general sort of guide. In general I think that the limonitic ores, unless they happen to be the sticky type, will give better performance than others in the furnace. At one time I thought that limonitic ores undergo extreme size degradation in the furnace. That is, they are soft and break down. That may be a contributing factor to the flue-dust production. But I rather think that some of the difficulty with limonitic ores has been due to the stickiness and upset distribution.

W. E. BREWSTER.—I question somewhat whether stickiness affects distribution. We use many ores that are sticky and do not have that trouble. When we used this particular ore we had difficulty immediately. I question whether the distribution was nearly as responsible as was the condition of the ore itself, with respect to combined moisture.

Could this method of yours be used to determine the nature of that kind of an ore? In other words, with your work could you determine about how that ore would perform, instead of going through the laborious and costly experiment of trying it in the furnace for a year or two?

W. A. HAVEN.—Mr. Brewster, will you permit me to answer for Mr. Joseph? You check me, Mr. Joseph, if I am not correct in my answer. It seems to me that Mr. Joseph's contention is that he will only predict the conduct of an ore as far as reducibility is concerned. As to what it will do mechanically, I do not believe he claims anything in that direction.

T. L. JOSEPH —That is right.

W. A. HAVEN.—Mr. Joseph has many of his results on the surprisingly good showing as to reducibility that has been made by the limonitic ores. A long time ago I was operating a furnace in western New York state. The bulk of our burden consisted of two very fine ores, Beaver and Cheever, just as bad for a blast furnace if used to excess as Tom and Jerry for a person, I suspect. One was a hematite and the other a magnetite from the eastern New York district, both very fine. Any blast-furnace man will easily understand that I had plenty of trouble.

In the ore yard there was a pile of limonitic ore—Davison ore. When operation became too difficult, I would take the Beaver and Cheever off temporarily and stick on a fairly good percentage of that limonitic ore; the furnace would smooth out and reduction would get better, the iron grade would be good and everything would be lovely for awhile. Unfortunately, I did not have enough to keep it up very long. The point that I wish to make is that the limonitic ore smoothed out the furnace, so that the thing that Mr. Hart was worried about, the limonite powdering up from its chemically combined water, evidently did not occur. It was easily reduced without excessive production of flue dust.

If you want to go further into this subject, take a trip to Europe and see what is being done with limonitic ore. It is being charged into the furnaces in pieces that are almost man size and less than 3000 lb of coke per ton is used on ores that run perhaps not over 28 or 29 per cent of iron content. Such practice can be attributed only to extreme reducibility of the ores. I have always wondered why such amazingly good results were obtained without crushing these ores. Mr. Joseph has offered a very nice explanation of it.

C. HART.—I am not worrying about the fineness of the limonite ores. That is what I like about them. They crack up and by the time they get down 30 ft in the furnace they present themselves in proper condition for reduction. They are too far down to come up badly as flue dust. The flue dust does harm at the top. I believe in using limonite to the limit.

W. A. HAVEN.—I think Mr. Brewster is talking about something that the rest of us are not very familiar with; that is, limonitic Mesabi ores.

F. H. CROCKARD —An average burden of a southern furnace would be 75 per cent of the hard ores we have been discussing and about 25 per cent of a brown ore, or limonitic ore. We have decided that 1 in. is the proper size for our hard ores, but if you are going to test you will find something different for the limonitic ores. However, if a sized hard ore is used it is necessary to use a limonitic ore of the same size in connection with it. It is a mechanical proposition of distribution.

W. A. HAVEN.—There is a segregation of sizes that is difficult.

R. H. SWEETSER,* New York, N. Y.—I want to add one point to Fig 6, showing the relation between porosity of iron ore and maximum size for blast-furnace use. In 1912, when Moose Mountain cobbled ore was put on the market, I was able to use 20 per cent of $\frac{3}{4}$ -in. Moose Mountain magnetite instead of 20 per cent Mesabi without making any change in the burden. That corroborates Fig. 6, and brings the size down to $\frac{3}{4}$ inch.

MEMBER —A year or two years ago there were discussions on reducibility of ores in relation to their iron silicate contents. In some of the ores containing iron silicates the reducibility was said to be very poor, but in actual practice they gave excellent results, particularly in regard to coke practice. Have you tried to correlate the two theories at all?

T. L. JOSEPH.—That work was on sinters. In studying the reducibility of sinters I found that two sinters practically the same as to porosity had a decided difference in reducibility. But, I found out, after I could determine or differentiate between the oxygen tied up with silicate and that which was magnetite, that I had a key to this difference: it was in the amount of iron silicate in the sample that retarded reduction. If there is iron silicate present it coats the grains of magnetite and retards the rate of reduction.

I did a little work on magnetites. The time required to reduce a cube of New York magnetite which had considerable silica in it, was about 10 times as long as the time required to reduce a cube of Provo ore, 40 min. as compared to 380. I do not think that is all due to iron silicate. I do not know certainly that there is iron silicate there. I have not determined it. There are differences due to the molecular structures. These magnetite ores had appreciable porosity, yet the order of reduction was entirely different. I do not believe this scheme or the relation between porosity and reducibility applies to magnetites. The Provo ore has about 12 to 20 per cent magnetite in it, but it is a different type of ore; it is what I call an altered magnetite; it has undergone some change that affects its reducibility.

I also tested a magnetite ore from New Mexico. That ore fitted the curve. These ores are different from the New York and the New Jersey magnetites. They look different and there is some difference in the character of the molecular structure that accounts for the difference in reducibilities.

Big pieces in an ore burden, pieces 4 or 5 in. in diameter, are a detriment. If those pieces are broken down into $1\frac{1}{2}$ or 2-in. pieces they will find a place in the

* Consulting Engineer.

burden where it needs opening. The big pieces roll into the furnace where it is probably already too porous. Smaller sizes are an aid in getting better gas distribution. That is more or less in line with Mr. Crockard's point.

MEMBER.—I wonder if from a physical-chemical standpoint we are not using porosity to mean something else? Is not reactivity a surface function, and are not the more porous ores more reducible because they give more surface where it is needed? I am merely adding this in order to go back to first principles instead of saying that porosity is only a measure showing the same amount of surface. A hard ore may have the same degree of porosity without having the same amount of surface exposed per unit weight. By "surface" I mean the actual surface that forms a gas where the gas can get to it to cause a reaction. My idea of reducibility is a function that is practically dependent upon the amount of gas surface exposed.

T. L. JOSEPH.—In general, I more or less assumed your point. That is, we know that heterogeneous reactions, or reactions between gaseous and solid phases, proceed at rates proportional to the surface. We must also keep in mind that reduction starts at the periphery of a sample. Metallic iron is formed at the surface, and if it is a porous ore there will be gradations from metallic iron at the surface on through FeO, magnetite, and hematite at the center. If the ore is dense reduction proceeds along a rather narrow band. The gas must get into the interior of the particle by diffusion. There is a surface around the boundary of the pores but the element of diffusion must be considered as well as the surface.

With a very dense ore, reduction starts at the surface. I have never proved this, but I think it could be done easily. The zone in which reduction is going on, reduction of iron in any degree of oxidation, either of FeO, hematite or magnetite, is rather narrow and this narrow zone of reduction must be extended on toward the center of the lump.

C. H. HERTY, JR.,* Bethlehem, Pa.—This last question opened up a way for me to mention something. On page 80 is the statement that the actual rate determined by reduction with hydrogen would differ from those determined with CO, but the order of reducibility would be about the same. Have those tests been done with CO? If so, what was the difference in the order of reducibility, primarily from this standpoint? If the rate of reducibility was determined with CO in the same way as with hydrogen a good picture could be obtained of the true mechanism of reduction of iron ores, because diffusion should be at a different rate on account of the density of the gas.

T. L. JOSEPH.—I have never gone into the question of carbon monoxide reduction. After all, we can determine only relative reducibility. I have gone to furnace conditions to check my results, but I think your point is well taken that perhaps it would be possible, by using CO and hydrogen, to get some idea as to the importance of diffusion due to the difference in the molecular weight of hydrogen, although I think the water molecule would be the one to consider; that is, the water molecules and the CO₂ molecules.

R. S. DEAN.—I do not think that we want to confuse what might be called an engineering determination with the physical chemistry of the situation. There has been a rather recent investigation of iron oxide reduction in Germany. I cannot remember the reference at the moment. It has been shown rather conclusively that whether production of iron is by reduction of Fe₂O₃ or FeO depends on the tempera-

* Bethlehem Steel Co.

ture, and whether there is hydrogen and CO or not. There are instances of production from Fe_2O_3 to iron as far as the X-ray determinations are concerned. It involves many complications. Mr. Joseph has something that correlates with furnace practice, and that is what he is aiming at. Here is something that gives an idea of what happens in the furnace from the engineering standpoint. It is like the tensile strength used in physical metallurgy.

W. A. HAVEN.—That is important. I should like to testify, for Mr. Joseph's benefit, that as consulting engineers we have been using his reducibility tests for the purpose of forecasting the conduct of ores, particularly those in foreign countries that we have been asked to pass upon and evaluate.

In this country a shipment of ore can be tried out in practice. When a carload of ore is in China, however, or some other remote place, distant from a blast furnace, it is not so easy. It is often almost impossible to say, from looking at the ore and examining it chemically, what its reducibility will be. But with the aid of Mr. Joseph's test we have not only been able to predict rather closely the amount of coke that would be needed to reduce a certain ore, but also establish the amount of crushing that would be necessary to make that ore a good furnace burden.

I have the following statement by one of our firm's engineers, Mr. Miller.

J. R. MILLER,* (Cleveland, Ohio (written discussion))—Mr. Joseph's paper concisely answers many questions that have arisen in the application of reducibility tests to specific ores which had not been subjected to metallurgical operations but the relative suitability of which it has been desirable to estimate. The careful experimental work described has definitely indicated porosity as the principal physical quality influencing reducibility and has developed methods for the determination of the average porosity on representative bulk samples, which should prove more satisfactory than the evaluation of the average physical condition of the ore by expert examination; however, as mentioned, certain ores are not amenable to reliable tests for effective porosity, it being indicated by chemical composition, tendency to disintegration, etc., the reducibility tests completing the picture in these cases.

Thus we now have the reducibility tests on definite specimens to determine the relative reducibility of the specimens and the porosity tests to correlate the results with the average condition of the ores, which in the hands of persons sufficiently familiar with ores should provide the means for determining the relative suitability of the ores and also, as stated in the paper, the size to which each type of ore should be crushed before it is charged into the blast furnace.

G. D. RAMSAY,† Provo, Utah (written discussion)—One cannot help being deeply impressed in reviewing this paper by the thought that the results obtained in the investigation again indicate the close interdependent relationship of the reducibility of an ore and its size as charged upon the final thermal efficiency of the blast furnace. Prior to the investigations of the Bureau of Mines, furnace operators were inclined to view the effect of the size of the ore and its reducibility independently. If an operator were confronted with a hard ore of low porosity he knew he could effect fuel economies by crushing. On the other hand it was early recognized that sintering of extremely fine portions of the blast-furnace burden produced lower coke rates. It was the writer's good fortune to be on the blast-furnace operating staff at the South Chicago plant of the Illinois Steel Co. at the time that included the investigation of the Bureau of Mines and later to be in charge of the Ironton blast furnace of the Columbia Steel Co., which previously had been investigated by the Bureau. Inasmuch as the South Chicago furnaces use a high percentage of soft, fine, Mesabi

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† Blast Furnace Superintendent, Ironton Works, Columbia Steel Co.

hematites and the Iron-ton furnace uses 100 per cent hard, compacted ore containing semialtered magnetites, they may be said to represent almost the extremes in the types of ores used.

As a result of the investigation of the Bureau of Mines the ore for the Iron-ton furnace is crushed and screened into three sizes: 30 per cent minus $2\frac{1}{4}$ plus $1\frac{1}{4}$ in; 30 per cent minus $1\frac{1}{4}$ plus $\frac{3}{8}$ in; 40 per cent minus $\frac{3}{8}$ in. Even crushing the ore without screening into sizes had previously reduced the fuel consumption appreciably. Naturally the separation by screening and the separate charging of each size of ore increased still further the furnace efficiency, showing a CO:CO₂ ratio as low as 1.4. All of these measures had been dealing with the reducibility factor of the ore alone. In other words, an ore with what might be termed a high reducibility index, or conversely a low porosity index, had been benefited by compensating for this factor by crushing and screening, thus increasing the gas-solid contact in the furnace.

At this point practical operating difficulties were encountered. Higher blast pressures prevailed and periods of irregular movement of the blast-furnace stock column increased. More flue dust was produced. All these were common indications of a stock column too tight for a free passage of the ascending gases. In other words, the practical limit in crushing had been exceeded without further beneficiation of the fine ore. Sintering equipment was then built so that all of the minus $\frac{3}{8}$ -in ore is now sintered. Immediate correction of the operating difficulties mentioned has been obtained.

It should not be inferred from the foregoing that the sizing of the ores for the Iron-ton blast furnace is absolutely correct. They have only been crushed to a size the largest of which was associated with so many fines that these in turn necessitated sintering to obtain the best combined effect in the blast-furnace burden. It is at least the opinion of the operating staff at Iron-ton that the size of the largest ore particle is still too large for best thermal efficiency, particularly from the standpoint of the small free-burning porous coke used as fuel. This opinion should be confirmed by an investigation similar to the one previously conducted by the Bureau of Mines on the same furnace. Unfortunately economic conditions have not permitted full operating schedules on the furnace since the introduction of sintered ore in the burden, so that comparable investigations have not been possible.

For the reasons just mentioned, it is doubtful whether the optimum size ore is now used at Iron-ton and Mr. Joseph's use of this ore in establishing ore sizes at other plants is probably not fully justified. It would also seem advisable to differentiate between the effect of crushing alone and that of crushing and separating into separately charged sizes when using the results on the Iron-ton furnace as a criterion.

If, from the standpoint of reducibility of ores, it is deemed advisable to crush and screen to the point of producing fines that must be sintered, further investigations on the porosity and reducibility of sinters themselves seem to be indicated. Today, sinters being charged to the blast furnaces over the country vary from weak, friable types to hard and apparently more irreducible nodules. From results at Iron-ton it is further possible that sinter should be sized and separately charged in the same manner as the ore. Further research should develop a guide for the alignment of this practice.

Dr. C. C. Furnas himself, associated with the Bureau of Mines during its earlier period of investigation of blast-furnace phenomena, in his recently published book, "The Next Hundred Years," challenged the industry with the statement that basically the blast furnace is the same today as it was at its inception. Papers such as this by Mr. Joseph and others by workers in the Bureau do indicate the way in which immediate improvements in blast-furnace practice can be made by the beneficiation and preparation of the raw materials even though the furnaces themselves need not be radically redesigned overnight.

Relative Desulfurizing Powers of Blast-furnace Slags

BY W. F. HOLBROOK* AND T. L. JOSEPH,† MEMBER A.I.M.E.

(New York Meeting, February, 1936)

THE problem of sulfur control is important in all blast-furnace operations but particularly for certain grades of steel because of the rigorous specifications. During the past decade the tendency has been to produce pig iron and hot metal of lower sulfur content. As most of the sulfur in the iron originates in the fuel, the use of high-sulfur coke demands modifications in practice to meet sulfur specifications.

While it is generally known that high temperatures and more basic slags favor desulfurization, operators as a rule produce the most acid slag that will permit proper desulfurization. The viscosity of blast-furnace slag has been thought to be related to desulfurization and has been investigated by Feild and Royster¹, also McCaffery and his associates², but apparently no systematic effort has been made to determine the relative desulfurizing powers of slags over the range of composition encountered in practice.

DEVELOPMENT OF TESTING METHOD

Because slag and metallic iron are immiscible, the desulfurization reaction is heterogeneous, occurring only at the interfaces between slag and metal bodies. In the blast furnace the newly reduced iron, containing FeS, descends through the slag bath probably either as small drops or streams, at the interfaces of which desulfurization occurs. After its descent through the slag the iron collects to form a bath of metal, at the top surface of which desulfurization reaction probably occurs. These two steps have been thought to account for all desulfurization in the blast furnace. Kinney³ found that metal removed from the blast furnace just above the tuyeres contained three to four times as much sulfur as the iron at cast. Herty and Gaines⁴ conclude that most of the sulfur is removed while the metal is passing through the slag. Mund, Stoecker

Manuscript received at the office of the Institute Dec. 2, 1935. Published by permission of the Director, U.S. Bureau of Mines.

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and Eilender⁵ show that the critical removal of sulfur occurs below the tuyeres.

In this investigation it was planned to use tests that would simulate desulfurization both by falling drops and quiet baths. Previous work by Wood and Joseph⁶ had involved both types of tests and partly pointed the way in the development of the present tests. Desulfurization by falling drops at blast-furnace temperatures proved impracticable for laboratory measurement. Discharge of metal through nozzles ranging from 0.040 to 0.144 in. in diameter produced drops ranging from approximately 0.04 to 0.25 in., the diameter of the average drop being proportional to the nozzle diameter. Metal discharge through such nozzles and into crucibles containing a 5-in. column of slag reached the bottom of the slag bath quickly and with little loss of sulfur. Usually some metal was found at the top of the slag bath as drops, but most of it reached the bottom of the crucible. Surface tension probably prevented descent of the droplets until by coalescence they became heavy enough to rupture the slag surface, whereupon they descended rapidly.

Other schemes were tried to increase the period of contact between the slag and the descending metal, including the use of coke immersed in the slag to induce a tortuous passage of the metal and the use of a spiral graphite guide to increase the distance of travel. These tests were unsuccessful, owing to the difficulty of reproducing conditions or to the extreme slowness of the resulting movement of metal through the slag bath.

It appeared that conditions would be more reproducible with the quiet-bath type of test. It seemed also that this type of test would be similar to the falling-drop type in that desulfurization must occur in both across an interface between metal and slag. The essential difference between the two types of desulfurization is that CaS is washed away from the surface of a moving drop but tends to accumulate at the surface of a quiet bath. It will be shown, however, that a truly quiet interface does not exist during desulfurization and that the quiet-bath tests assumed some of the characteristics of falling-drop tests.

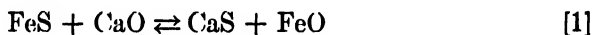
Preliminary tests led to the adoption of the following conditions as standard for the investigation: (1) Temperature, 1500°C . (2732°F .), which is within the customary blast-furnace range; (2) charge, 12 grams of metal and 5 grams of slag, making approximately equal volumes of metal and slag; (3) sulfur, 0.8 per cent in the metal charged, as this quantity produces slags of typical sulfur content; (4) duration of test conditions, 30 min., which is sufficient for some desulfurization with an ordinary slag and short enough so that equilibrium is not reached with even the best slags, thereby permitting comparisons to be made. Melts were made in $\frac{5}{8}$ by 2-in. holes, six of which were equally spaced

as near as practicable to the wall of a $2\frac{1}{4}$ by $2\frac{1}{4}$ -in. piece of electrode graphite rod. One control charge was included in each heat of six charges, so that the existence of abnormal conditions affecting the desulfurizing power of slags could be detected.

Tests were made in an induction furnace 18 in. high and $2\frac{3}{8}$ in. in internal diameter. These dimensions assured a central zone of uniform temperature into which the crucibles were placed. Temperature measurements were made in early tests by sighting with an optical pyrometer on the mirror image of the bottom of the crucible through a shutter in the lower part of the furnace. Later measurements were made with a tungsten-graphite thermocouple extending through the bottom of the furnace and arranged so that the crucibles used for the tests rested on the tip of the thermocouple. In both tests frequent calibrations were made against a noble-metal thermocouple, and the desulfurization observed for the control slag served as a temperature check from run to run.

MECHANISM INVOLVED IN MOVEMENT OF SULFUR THROUGH SLAG

The desulfurization reaction



is reversible, and the products, CaS and FeO, tend to accumulate in the reaction zone, thus retarding the rate of the reaction. The tendency for a high-sulfide film to form at the interface between slag and metal is shown clearly in Fig. 1. These are sulfur prints made from solid specimens of slag and metal that had been heated previously to a desulfurizing temperature. Sulfur prints are made by pressing photographic paper that has been moistened by immersion in dilute H_2SO_4 against



Fig. 1.—ACCUMULATION OF CaS AT INTERFACE.

the flat, ground surface of the object to be printed. Wherever there are soluble sulfides in the object, brown stains are formed on the paper, and the intensity of the stain varies with the concentration of the sulfide. The spotted or granular appearance of the part of the print that was in contact with the metal is due to the segregation of sulfide in the solid iron. The cross section of metal is bounded above by a very fine but distinct dark line caused by a high CaS film in the region of the interface. Above this is a small, evenly darkened area representing slag containing dissolved CaS.

Removal of CaS from the area of the interfacial film has been thought to depend on the slow process of diffusion⁷. Some of the FeO formed by the reaction of equation 1, however, is reduced immediately by the action of carbon dissolved in the iron:



The CO, formed at the interface, expands greatly at the prevailing temperature and readily assumes the form of bubbles, which, to escape, must cause configurations and movements in the metal and slag about them, particularly in the interfacial film. That this is true is illustrated by the sulfur print in Fig. 2, which was made from a quickly chilled specimen. This print shows a bubble of CO leaving the interfacial zone. The bubble is outlined by a part of the high-sulfide film in which it was formed. The movement of the bubble had distorted the film and was removing some of the CaS at the moment of solidification to some point within the slag bath. As such a bubble rises through the slag bath probably it leaves a trail of CaS, which then spreads by diffusion and by the movement of other bubbles. Thus, it is evident that diffusion alone need not account for the removal of CaS from the interface between the slag and metal baths.



FIG. 2.—BUBBLE OF CO OUTLINED BY FILM OF HIGH-SULFIDE SLAG.

FORMATION OF METAL DROPS IN QUIET BATHS

After the desulfurizing treatment of quiet baths of metal and slag, beads of metal were usually found at the top and sidewall surfaces of the slag. Sulfur printing of chilled specimens brought out two significant facts: (1) Metal beads were never found above the metal bath if the metal as charged contained no sulfur; and (2) metal beads found in the slag were always shown by the prints to be free of sulfur or very low in sulfur. It must be concluded therefore that movement of metal into the slag bath depends on desulfurization, and that the metal enters the slag in units that are small enough to be quickly desulfurized. The evolution of CO at the slag-metal bath interface furnishes conditions somewhat similar to those necessary for flotation. Fig. 3 shows the buoyant effect of the CO bubbles. It is a photograph (enlarged 21½ times) of a chilled specimen showing part of the surface of the metal bath and a vertical cross section through the slag bath of a test charge. Two distinct cavities may be seen in the slag body immediately above the

interface. Below each is a semispherical bead of iron, buoyed up somewhat above the level of the metal bath at the moment of solidification. Scattered about the surface of the main body of metal can be seen other beads of various sizes, each of which was probably produced by its corresponding gas bubble.

Further evidence that the presence of beads of metal in the slag bath is associated directly with desulfurization is seen in Fig. 4, which shows three specimens of slag and metal from which parts of the graphite containers have been broken away to reveal the surfaces of the specimens. The slag charged in the three specimens was of uniform composition. The metal contained 1.7, 0.7, and 0.01 per cent sulfur, respectively. These charges were subjected to a temperature of 1500° C. (2732° F.) for 10 min. and then chilled. The movement of metal into the slag varied with the amount of sulfur in the metal, the specimen on the right showing no interfacial disturbance because there was no desulfurization and no evolution of CO.

Several specimens were prepared for sulfur printing by grinding through the side of the graphite container to expose a surface of the slag with metal bodies in place. Figs. 5 and 6 show one such specimen and the print made from it. The latter shows that the large beads of metal in the slag are low in sulfur. There are no cavities in the slag above these beads, showing that the beads were not being raised at the moment of solidification. Rather, they seem to be on a return trip to the metal bath.

The following hypothetical cycle accounts for the observed phenomena. At the interface between the slag and metal bath a bubble of CO is formed according to the desulfurization reaction. The bubble remains attached to the metal bath until it grows so large that its buoyancy in the slag causes it to separate from the metal bath and rise through the slag. The separation is not perfect, however, and as the CO bubble rises there is attached to it a very small drop of metal, which, because of its size, is quickly and thoroughly desulfurized. At the top surface of the slag the bubble bursts, releasing the droplet, which, by coalescence with other droplets, becomes heavy enough to fall back through the slag to



FIG. 3.-- SECTION OF CHILLED SPECIMEN ILLUSTRATING BUOYANT EFFECT OF EVOLVED CO.

the metal bath. There it mixes with the bath metal, lowering the sulfur content of the bath but reducing the speed of desulfurization as well. Fig. 7 shows a number of the minute, spherical, metal particles removed from a sample of slag crushed to pass a 100-mesh screen.

Metal containing 0.1 per cent sulfur has a potential lifting power, by means of the CO it can liberate, of more than nine times the weight of the

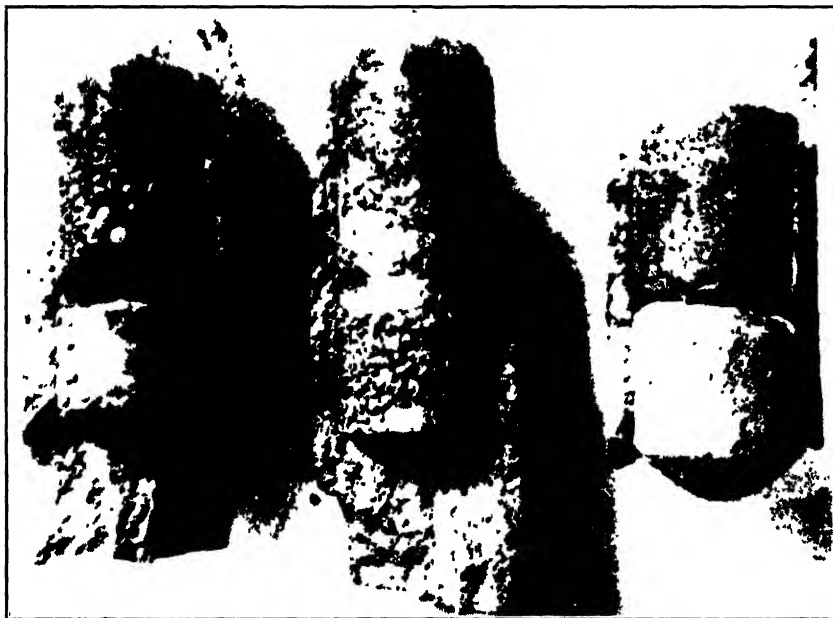


FIG. 4.—SPECIMENS SHOWING MOVEMENT OF METAL INTO SLAG BATH BY DESULFURIZATION REACTION.

Metals contained 1.7, 0.7 and 0.01 per cent sulfur, respectively.

metal. If used efficiently this power could cause the metal to make nine trips through the slag. Only one trip is required to remove the sulfur from a single metal particle, but the potential lifting power of the particle is also removed. On its return to the metal bath the desulfurized metal mixes with the undesulfurized metal; thus, as the process progresses its efficiency decreases.

The preceding discussion explains the desulfurization phenomena in the tests. Most of the desulfurization in the blast furnace is thought to occur as the newly reduced metal descends from the plane of the tuyères to that of the metal bath and very little at the surface of the metal bath. Desulfurization of metal drops as they pass through the slag would seem to be favored by a high viscosity, which would prolong the period of contact. Yet low viscosity is thought by many to be essential to rapid desulfurization. Desulfurization of the falling drop would probably result in evolution of CO, the buoyancy of which would prolong the

period of descent even in a fluid slag. Thus, phenomena observed in the tests may, to a degree, apply in blast-furnace desulfurization. The fact that many of the effects of composition change, as shown by the tests, are confirmed by blast-furnace experience seems to justify the use of this type of test in a survey of the relation between slag composition and desulfurization.

It has been customary to speak of a slag's desulfurizing power in terms of basicity. The several definitions of the term show that no general and consistent relation exists between basicity and desulfurization. Therefore, it is desirable to survey the comparative desulfurizing powers of all blast-furnace slags that are likely to occur.

SCOPE OF PRESENT SURVEY OF DESULFURIZING POWERS OF SLAGS

The following range of slag composition is reported in this paper: 30 to 50 per cent SiO_2 , 5 to 25 per cent Al_2O_3 , 35 to 55 per cent CaO (all in steps of 2 per cent), and 0, 5 and 10 per cent MgO . For comparison the relative desulfurizing powers of the slags have been defined as the ratio of the percentage of sulfur in the slag to the percentage of sulfur in the metal at the end of the prescribed test.

It has proved practically impossible to hold all conditions constant, as shown by certain irregularities in the data obtained. Duplicate samples tested in one heat usually gave consistent results. Thus four samples of the control slag desulfurized simultaneously gave desulfurization ratios of 2.7, 2.7, 2.8 and 2.5, or an average value of 2.67. Variations observed from heat to heat are thought to have been due to temperature variations or possibly to differences in rates of heating and cooling. It is a well-known fact that the desulfurizing power of a slag varies greatly with temperature⁸. Although this variation with temperature may not be proportional over a wide temperature range, it may be considered to be proportional over the narrow range of temperature change encountered during the tests. To compensate for the small variations in the test conditions, the desulfurization ratio observed for each slag was



FIG. 5.

FIG. 6.

FIG. 5.—CROSS SECTION OF SPECIMEN SHOWING BEADS OF METAL IN SLAG BODY.

FIG. 6.—SULFUR PRINT MADE FROM SPECIMEN SHOWN IN FIG. 5.

multiplied by the factor necessary to bring that of the control slag to 2.7. This procedure evidently was justified, as consistent data were obtained.

PREPARATION OF SLAGS

Slags of the desired compositions were synthesized by adding suitable amounts of pure oxides to portions of slags of known composition. Thus each charge consisted of a large proportion of a previously fused, powdered



FIG. 7.—METAL DROPLETS REMOVED FROM CRUSHED SLAG FROM DESULFURIZATION TEST. $\times 44$.

slag intimately mixed with a smaller proportion of pure oxides, the desired slag being formed in place when the necessary temperature was attained. It was found unnecessary to premelt the mixture, the same desulfurization ratio being obtained from premelted and freshly mixed charges. This difference in experience from that of other investigators of viscosity is probably due to the smaller volume of slag used in the desulfurization tests.

As the representation of a four-component system by an equilateral tetrahedron cannot be shown easily on a flat page, the data have been recorded on planes representing slags of a uniform MgO content. Each plane is a part of a triaxial diagram of which the apexes represent 100 per cent SiO_2 , 100 per cent Al_2O_3 , and 100 per cent CaO plus MgO. Iso-desulfurization lines have been drawn through points of equal desulfurizing powers on each plane. On each diagram the effect on desulfurization of changing any of the three components, SiO_2 , Al_2O_3 and CaO , may be observed. For slags representing 0, 5 or 10 per cent MgO, the desulfurization ratio may be seen directly on the diagram. For intermediate MgO contents proportionate values may be assumed because the changes in desulfurizing power with composition generally are gradual and progressive.

PRESENTATION OF DATA

MgO-free Slags.—The relative desulfurizing powers of MgO-free slags as determined for 30 to 50 per cent SiO_2 , 5 to 25 per cent Al_2O_3 , and 35 to

TABLE 1.—*Comparative Desulfurizing Power of Slags Containing No MgO*

Composition, Per Cent				Composition, Per Cent			
SiO ₂	Al ₂ O ₃	CaO	R*	SiO ₂	Al ₂ O ₃	CaO	R
50	5	45	1 6	40	15	45	3 5
	7	43	1 3		17	43	3 3
	9	41	1 1		19	41	2 4
	11	39	0 9		21	39	2 0
	13	37	0 8		23	37	1 4
	15	35	0 6		25	35	1 0
48	5	47	2 7	38	7	55	7 5
	7	45	2 1		9	53	11 3
	9	43	1 8		11	51	9 6
	11	41	1 4		13	49	7 4
	13	39	1 2		15	47	5 2
	15	37	0 9		17	45	4 4
46	17	35	0 8		19	43	3 3
	5	49	3 8		21	41	2 5
	7	47	3 1		23	39	1 9
	9	45	3 0		25	37	1 7
	11	43	2 0	36	9	55	3 2
	13	41	1 6		11	53	13 4
44	15	39	1 3		13	51	9 3
	17	37	1 0		15	49	7 1
	19	35	0 8		17	47	5 9
	5	51	6 0		19	45	4 6
	7	49	5 0		21	43	3 5
	9	47	4 1	34	23	41	3 0
42	11	45	3 0		25	39	2 4
	13	43	2 2		11	55	3 8
	15	41	1 6		13	53	5 9
	17	39	1 3		15	51	12 2
	19	37	1 0		17	49	9 6
	21	35	0 8		19	47	6 3
40	5	53	6 7	32	21	45	6 2
	7	51	6 9		23	43	4 6
	9	49	5 4		25	41	3 3
	11	47	4 8		13	55	1 4
	13	45	3 6		15	53	2 4
	15	43	3 0		17	51	13 7
40	17	41	2 5	30	19	49	11 1
	19	39	1 9		21	47	7 5
	21	37	1 4		23	45	5 4
	23	35	1 1		25	43	3 3
	5	55	9 6		15	55	0 9
	7	53	9 6		17	53	1 5
40	9	51	7 5	30	19	51	5 9
	11	49	6 4		21	49	6 2
	13	47	5 2		23	47	6 9
					25	45	3 9

* $\left(\frac{\text{Per cent S in slag}}{\text{Per cent S in metal}} \right)$

55 per cent CaO, are given in Table 1. These are actual experimental values. The isodesulfurization lines in Fig. 8, representing these data, have been modified to eliminate a slight waviness due apparently to experimental error. The isodesulfurization lines are nearly parallel over most of the area shown. Their values increase regularly and rapidly

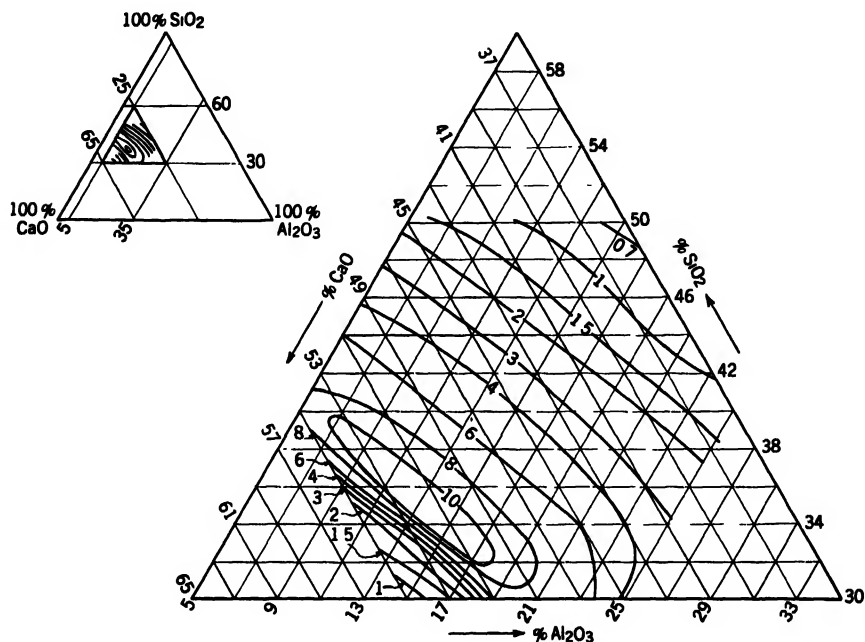


FIG. 8.—COMPOSITION-DESULFURIZATION DIAGRAM OF SLAGS CONTAINING NO MgO .

as CaO replaces SiO_2 , less rapidly as CaO replaces Al_2O_3 , and slowly as Al_2O_3 replaces SiO_2 . An area of optimum desulfurization composition appears near the lower left portion of the diagram, representing slags of approximately 51 per cent CaO and 10 to 18 per cent Al_2O_3 . As CaO content or basicity is increased beyond this area, the desulfurizing power of the slag falls rapidly.

The isodesulfurization lines are not parallel to any of the composition axes, except over a very narrow range. If they were parallel to the CaO axes, for instance, it would signify that Al_2O_3 and SiO_2 were interchangeable on a weight basis without change in desulfurizing power. As composition change is traced in the direction of increasing CaO content along either an SiO_2 axis (constant SiO_2) or an Al_2O_3 axis (constant Al_2O_3) isodesulfurization curves of increasing values are crossed. Thus, over the range shown by most of the diagram, CaO has a positive effect on desulfurization. Proceeding across the diagram along a CaO axis (constant CaO) one encounters a slowly increasing desulfurizing power. This indicates that the desulfurizing qualities of a slag improve as Al_2O_3

replaces SiO_2 . This effect does not hold true in the range represented by the lower part of the diagram where the slags increase rapidly in viscosity.

How to Use the Diagram.—As an example, assume that a certain slag has 39.4 per cent SiO_2 , 14.5 per cent Al_2O_3 , and 46.1 per cent CaO . The point on the diagram (Fig. 8) representing this slag lies between isodesulfurization lines having values of 4 and 6. The approximate value would be 4.9. Raising the Al_2O_3 to 17.0 per cent and lowering the SiO_2 to 36.9 per cent would favor desulfurization, because the relative desulfurizing value of the resulting slag would be about 5.8. If the increase in Al_2O_3 occurred at the expense of CaO , however, the slag would

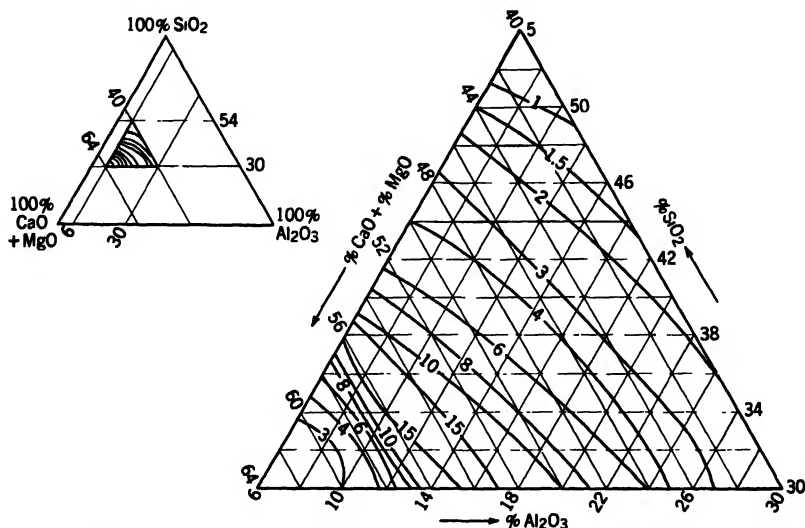


FIG. 9.— COMPOSITION-DESULFURIZATION DIAGRAM OF SLAGS CONTAINING 5 PER CENT MgO .

have a relative desulfurizing value of 3.7, as shown by the diagram for a slag containing 17.0 per cent Al_2O_3 and 43.6 per cent CaO .

Assume that another slag, whose desulfurizing power is 10, is composed of 35.8 per cent SiO_2 , 11.0 per cent Al_2O_3 and 53.2 per cent CaO . To what extent can the SiO_2 be varied, keeping the Al_2O_3 constant, without lowering the desulfurizing value more than two units? The isodesulfurization curve having a comparative value of 8.0 crosses the 11 per cent Al_2O_3 line at SiO_2 contents of 35.6 and 38.7 per cent. Thus this slag is at the border of a critical composition range. A decrease of 0.2 per cent of SiO_2 with an increase of 0.2 per cent CaO causes the same lowering of desulfurizing power of the slag as a change of 2.9 per cent in the other direction.

The effect on desulfurization of adding one oxide to a slag of a given composition without changing the ratio of the other two can be deter-

TABLE 2.—*Comparative Desulfurizing Power of Slags Containing 5 Per Cent MgO*

Composition, Per Cent				Composition, Per Cent			
SiO ₂	Al ₂ O ₃	CaO	R ^a	SiO ₂	Al ₂ O ₃	CaO	R ^a
50	6	39	1 5	36	6	53	8 5
	8	37	1 2		8	51	18 4
	10	35	0 9		10	49	13 1
48	6	41	2 1		12	47	9 8
	8	39	1 9		14	45	7 5
	10	37	1 4		16	43	5 9
	12	35	1 1		18	41	4 1
46	6	43	3 2		20	39	3 0
	8	41	3 1		22	37	2 9
	10	39	2 1		24	35	2 4
	12	37	1 7	34	6	55	3 4
	14	35	1 3		8	53	2 8
44	6	45	4 0		10	51	19 0
	8	43	3 4		12	49	14 0
	10	41	2 6		14	47	11 1
	12	39	2 1		16	45	7 4
	14	37	1 6		18	43	5 9
	16	35	1 3		20	41	4 6
42	6	47	5 5		22	39	3 6
	8	45	4 6		24	37	3 0
	10	43	4 1		26	35	2 3
	12	41	3 0	32	8	55	2 7
	14	39	2 7		10	53	6 5
	16	37	2 0		12	51	13 0
	18	35	1 7		14	49	16 0
40	6	49	8 8		16	47	11 4
	8	47	6 8		18	45	9 2
	10	45	5 7		20	43	7 0
	12	43	4 4		22	41	4 8
	14	41	3 0		24	39	3 0
	16	39	2 6		26	37	2 6
	18	37	2 1	30	10	55	3 0
	20	35	1 6		12	53	1 6
38	6	51	17 0		14	51	13 0
	8	49	10 0		16	49	23 0
	10	47	7 7		18	47	11 4
	12	45	5 5		20	45	10 0
	14	43	4 7		22	43	7 2
	16	41	3 3		24	41	6 7
	18	39	2 8		26	39	3 7
	20	37	2 4				
	22	35	1 8				

^a $\left(\frac{\text{Per cent S in slag}}{\text{Per cent S in metal}} \right)$.

mined by moving in the direction of 100 per cent of the oxide added. This direction may be found by inspection of the pilot triaxial diagram.

5 Per Cent MgO Slags.—If the effects of MgO and CaO on desulfurization were identical, any quantity of one could replace an equal quantity of the other in a slag without changing the desulfurizing action, and one diagram would suffice for all changes in slag composition. The CaO axis on the diagram would then represent CaO plus MgO.

The data (Table 2) obtained in the investigation of 5 per cent MgO slags and the diagram prepared therefrom (Fig. 9) show that in acid slags 5 per cent of CaO may be replaced by MgO with little effect on

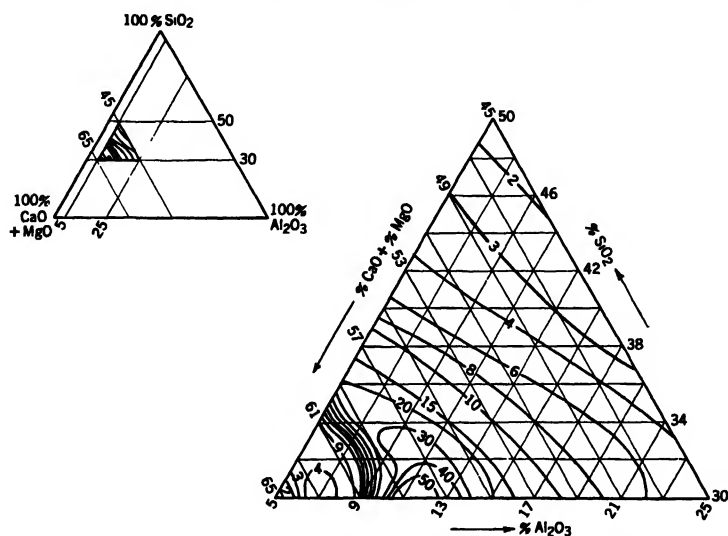


FIG. 10.—COMPOSITION-DESULFURIZATION DIAGRAM OF SLAGS CONTAINING 10 PER CENT MgO.

desulfurization. As the basicity is increased, however, the magnesian slags become less and less effective until the area representing an optimum composition for MgO-free slags is reached. As basicity is further increased over a range in which MgO-free slags rapidly lose their desulfurizing efficiency, the 5 per cent MgO slags continue to improve, reaching in their optimum range a desulfurizing value greatly in excess of the best MgO-free slags. This optimum range in composition occurs when the bases, CaO plus MgO, amount to about 55 per cent. At still higher basicities these slags also lose their desulfurizing efficiency rapidly.

The isodesulfurization lines in Fig. 9 follow practically the same slope as those in Fig. 8. Thus the effect of changes in Al_2O_3 and SiO_2 in 5 per cent MgO slags and MgO-free slags is very similar. Generally 5 per cent MgO slags are poorer desulfurizers than corresponding MgO-free slags, except over a small range of more basic composition where they are decidedly superior. The most significant effect then of 5 per

cent of MgO in desulfurizing slags is to permit the use of slags of more basic composition.

10 Per Cent MgO Slags.—Every statement made relative to the trends in the effect of 5 per cent MgO on desulfurizing slags may be extended to include slags containing 10 per cent MgO. The slope of the isodesulfurization lines is substantially the same; the optimum range is still more

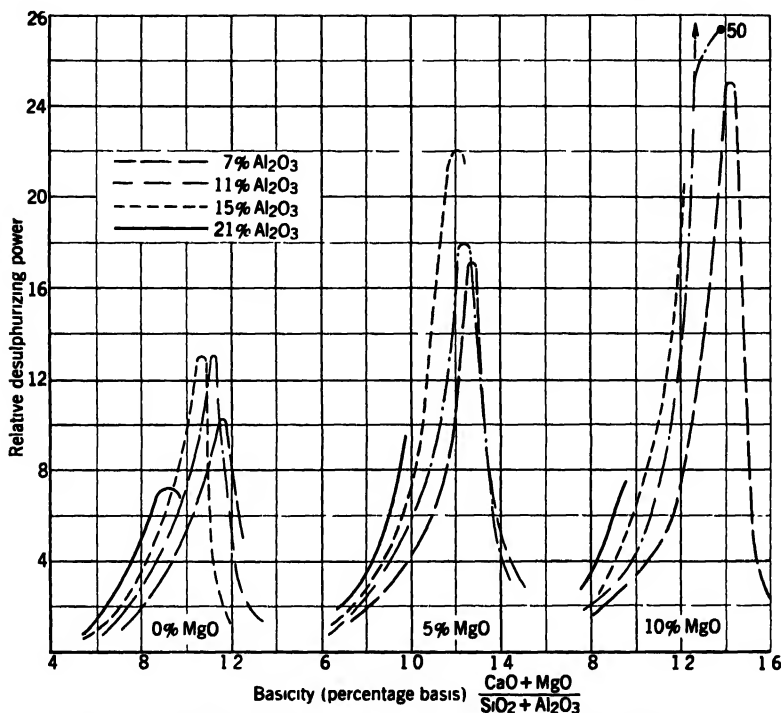


FIG. 11.—EFFECT OF Al_2O_3 ON BASICITY AND DESULFURIZATION.

basic, and the desulfurizing powers of the slags in the optimum range are still greater than the best observed for slags containing less MgO. Table 3 and Fig. 10 show that the best 10 per cent MgO slags, from the standpoint of desulfurization, occur when the bases, CaO plus MgO, total approximately 58 per cent.

In estimating desulfurization values for slags of intermediate MgO contents proportionate values may be assumed, as already pointed out. For example, an average slag might show the following analysis: 35 per cent SiO_2 , 13.9 per cent Al_2O_3 , 43.5 per cent CaO, and 4.0 per cent MgO. On a basis of 100 per cent of these four oxides, the composition would be 36.4 per cent SiO_2 , 14.4 per cent Al_2O_3 , 45.1 per cent CaO and 4.1 per cent MgO. Combining the bases to a total of 49.2 per cent, one finds that the desulfurizing ratio as indicated in the diagram for 0 per cent MgO is 8.3.

TABLE 3.—Comparative Desulfurizing Power of Slags Containing 10 Per Cent MgO

Composition, Per Cent				Composition, Per Cent				
SiO ₂	Al ₂ O ₃	CaO	R ^a	SiO ₂	Al ₂ O ₃	CaO	R ^a	
50	5	35	1 5	34	5	51	1 2	
48	5	37	2 2		7	49	26 0	
	7	35	1 7		9	47	23 0	
46	5	39	3 0		11	45	15 0	
					13	43	10 0	
					15	41	7 7	
44	7	37	2 4		17	39	6 5	
					19	37	4 5	
					21	35	3 7	
42	5	41	3 5	32	5	53	3 7	
	7	39	2 9		7	51	3.1	
	9	37	2 5		9	49	1 0	
	11	35	2 1		11	47	37 0	
40	5	43	4 3		13	45	24 0	
	7	41	3 8		15	43	12 0	
	9	39	3 2		17	41	9 1	
	11	37	2 7		19	39	7 0	
	13	35	2 3		21	37	5 9	
38	5	45	6 9		23	35	4 2	
	7	43	5 6	30	5	55	1 7	
	9	41	4 4		7	53	4 3	
	11	39	3 7		9	51	9 2	
	13	37	2 9		11	49	84 0	
	15	35	2 5		13	47	42 0	
36	5	47	11 5		15	45	21 0	
	7	45	10 6		17	43	13 0	
	9	43	7 8		19	41	9 2	
	11	41	5 5		21	39	7 9	
	13	39	4 7		23	37	5 3	
	15	37	3 5		25	35	4 8	
	17	35	3 1					

^a $\left(\frac{\text{Per cent S in slag}}{\text{Per cent S in metal}} \right)$.

On the 5 per cent MgO diagram the ratio is 6.3. The desulfurization ratio for the average slag then would be $8.3 - \left(\frac{4.1}{5.0} \times [8.3 - 6.3] \right) = 6.65$.

Slags with isodesulfurization lines of about 8 may therefore be considered to be of average desulfurizing power. The method of predicting the effect on desulfurization of any ordinary change in composition is evident from the examples given.

CONCLUSIONS

Basicity and Desulfurization.—The need of a simple formula to relate desulfurization to slag composition has long been felt. As a result of the strong effect of CaO on desulfurization, many have seen such a formula in "basicity." Various definitions of the term have been devised according to the observations of various individuals working with slags of limited range in composition. Basicity is frequently defined as the ratio of bases (CaO + MgO) to acids ($\text{SiO}_2 + \text{Al}_2\text{O}_3$). Fig. 11 shows basicity values,

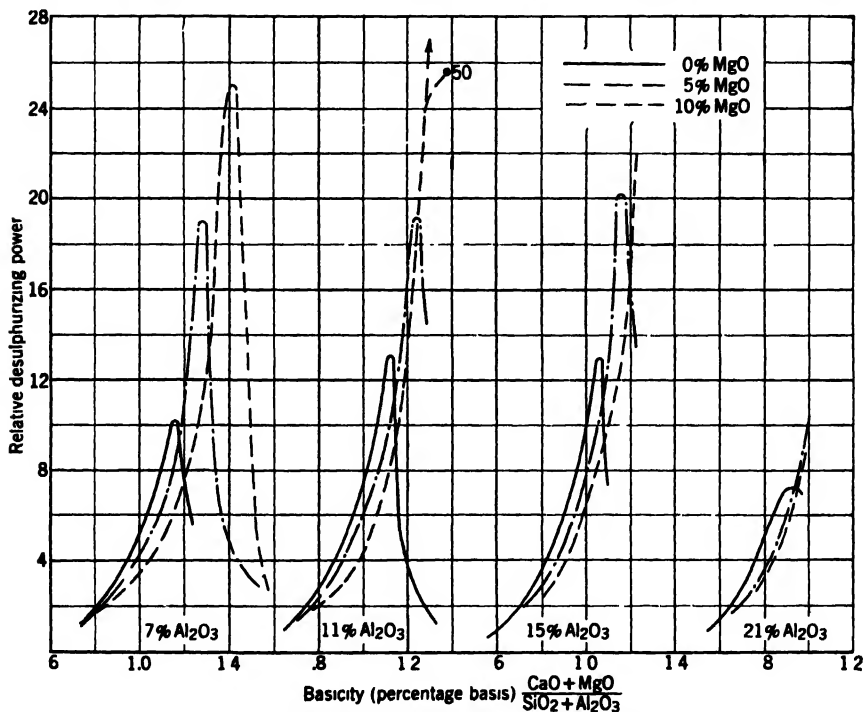


FIG. 12.—EFFECT OF MgO ON BASICITY AND DESULFURIZATION.

computed according to this definition, plotted against desulfurization ratios in groups of curves, each group representing a constant MgO content and each curve a constant Al_2O_3 content. Basicity does not fill all requirements as an index of desulfurization. Each curve, representing constant MgO and Al_2O_3 contents, shows a rising desulfurization characteristic with increasing CaO up to a certain point, beyond which the desulfurization ratio decreases rapidly. The falling desulfurization ratio occurs over a composition range in which viscosity increases abruptly. For any constant basicity (along the rising characteristic) an increase in the Al_2O_3 content of the slag thus increases its desulfurizing power. The effect of Al_2O_3 in increasing viscosity accounts for the earlier attainment

of maximum desulfurization and earlier rapid decline of desulfurization with increasing Al_2O_3 . The increase in desulfurization with an increase in Al_2O_3 content in the area of rising characteristics suggests the possibility that, within limits, high viscosity favors desulfurization.

The trends described apply in varying degree to slags of 0, 5 and 10 per cent MgO . The effect of MgO is demonstrated more clearly by Fig. 12, which shows the same curves grouped differently. Each group consists of curves of constant Al_2O_3 content, and each curve represents slags of constant MgO content. From this figure it is evident that along the rising characteristic increasing MgO results in decreasing desulfurization, but slags containing increasing amounts of MgO , owing to its thinning effect, attain higher basicities and therefore greater desulfurizing powers before the range of abrupt thickening is reached. Thus the most striking effect of MgO is to permit the use of higher basicity than would otherwise be possible.

Viscosity and Desulfurization.—It is interesting that in the plane of 0 per cent MgO the area of optimum desulfurization nearly coincides with the area of minimum viscosity as shown by McCaffery and coworkers². One might therefore conclude that the desulfurizing power of a slag is closely associated with its viscosity and that the viscosity data heretofore available are all that are necessary to forecast a slag's desirability as a desulfurizer. That low viscosity is not favorable to desulfurization is suggested by the fact that slags containing MgO , although usually less viscous, are generally poorer desulfurizers. Obviously there is some relationship between viscosity and desulfurization. For instance, a slag so viscous as to prevent any movement of metal through it is of no value as a desulfurizer. (See extreme lower left section, Fig. 8.) Thus, in this figure there are ranges of composition over which the relationship between viscosity and desulfurization is direct and other ranges over which the relationship is inverse.

The similarity between the isodesulfurization lines representing the 5 and 10 per cent MgO planes and the isoviscosity lines for corresponding slag compositions is less obvious than in the MgO -free slags. This fact tends to indicate that viscosity and desulfurization are not closely related.

Desulfurization and Temperature.—The data presented cover the relative desulfurizing power of various slags at a temperature of 1500°C . (2732°F .). Comparatively little work has been done on the effect of temperature change³. The results point to the fact that, except at temperatures near the melting point, the relative order of slags arranged according to their desulfurizing power remains unchanged with variation in temperature. The poor desulfurizing quality of slags below and to the left of optimum compositions in the diagrams is due to extreme viscosity. Such slags would have a much higher desulfurizing power at higher temperatures. Thus, the effect of raising the temperature would be to

raise the desulfurizing values of all slags, particularly the more basic and higher Al_2O_3 slags; that is, the area of optimum composition would be shifted downward and to the left. This effect of temperature change is illustrated as follows:

Al_2O_3 , PER CENT	PER CENT S IN SLAG	
	PER CENT S IN METAL 1500° C.	1550° C.
15	9 2	10 2
20	7 4	14 2
25	6 0	18 4

These data show the decreasing desulfurizing power of a slag at 1500° C. with increasing viscosity due to an increase in Al_2O_3 content and the rising desulfurization values at 1550° C. with the same increases in Al_2O_3 .

SUMMARY

A laboratory method has been devised by which the relative desulfurizing powers of slags of varying composition may be determined. Data and diagrams are presented showing relative desulfurizing powers at 1500° C. (2732° F.) of all blast-furnace slags containing 10 per cent or less of MgO that are likely to occur. No simple relationship was found by which chemical composition as designated by the term "basicity" could be compared with desulfurization. It is shown that to relate basicity and desulfurization MgO cannot be combined with CaO as "total bases," nor can Al_2O_3 be combined with SiO_2 as "total acids." Moreover, Al_2O_3 cannot be ignored in computing basicity, as is frequently done. Each oxide has its own effect on desulfurization, and the degree of the effect is not constant for all ranges of composition.

MgO has been found to be slightly deleterious to desulfurization of acid slags. The effect becomes increasingly undesirable as basicity is increased to that of slags of average composition. The presence of MgO , however, is decidedly favorable to desulfurization in the more basic slags.

It is suggested that the evolution of CO accompanying desulfurization has an important role of the over-all process. It retards the descent of falling metal drops and carries CaS and globules of metal away from the bath interface and into the slag, in both instances contributing to the effectiveness of the reaction.

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DISCUSSION

(William A. Haven presiding)

W. E. BREWSTER,* South Chicago, Ill.—Is this work all on one temperature basis?

T. L. JOSEPH—Yes, 2732° F. It is on the low side of the temperature range. However, we are going to study the effect of temperature. I should have brought that out more clearly.

W. E. BREWSTER—You must know the temperatures before you can refer your results to your charts. We have done considerable work along the line of Professor McCaffery's work in years past and have always run against the snag of not having the temperature and the analysis right there when we wanted it.

We have always found it much better to operate on a basicity formula of lime, plus magnesia, divided by silica. Our formula is practically fixed as we burden our furnace. The ratio varies from day to day, also from cast to cast, depending on the operation of the furnace, which includes the temperature and variations in the burden charge, such as it is at present. We have to refer in actual practice to the basicity ratio of lime plus magnesia over silica. No doubt the scheme can be worked out with your charts if you have them set up for certain temperatures in the operation. I think you have developed one of the simplest charts that has been shown yet to use in correlating slag compositions and sulfur in pig iron made on that particular slag.

F. H. CROCKARD,† Birmingham, Ala. (written discussion).—This paper is one of the most practical published to date on the effect of the constitution of blast-furnace slags. The three composition desulfurizing diagrams may be used to practical advantage by the blast-furnace operator, for they give definite values for something that has been the subject of much discussion. That the results apply to practical operation as well as the laboratory is indicated by the table on page 118.

The iron produced on the 27th had an average sulfur of 0.030 per cent if the figures of the chart are correct, the sulfurs on the 21st should average 0.023. They actually averaged 0.020 per cent, but this variation can easily be explained by the difference in silicon, it being 3.38 per cent on the 27th and 3.52 per cent on the 21st. The furnace operation was very regular at this time, so that the actual analysis varied very little from the averages indicated.

* Superintendent of Blast Furnace Dept., Wisconsin Steel Works, International Harvester Co.

† Metallurgist, Republic Steel Corporation.

	Slag 12/27		Slag 12/21	
	Actual	Converted to 100 Per Cent	Actual	Converted to 100 Per Cent
SiO ₂ .	36 00	36 90	36.00	36 80
Al ₂ O ₃	16 10	16.50	16 60	17 00
CaO	38 56	39 50	42 60	43 60
MgO	6 93	7.10	2.55	2.60
	97 59	100 00	97 75	100.00
Desulfurizing power		3 8		5.0

On another occasion, when making basic iron, a slag with magnesia content of 11 per cent with desulfurizing power of 3 gave considerable trouble with sulfur content of the iron, but when the magnesia was reduced to 5 per cent (keeping total bases the same) the desulfurizing power was increased to 5, and satisfactory iron was produced.

From these and similar observations from time to time, it seems that the laboratory observations as reported in the paper are substantiated by actual furnace slags, and the authors are to be commended for giving furnacemen a very practical guide

A. L. FEILD, New York, N.Y.—If you mean, in speaking of the thinning action of magnesia, a change toward a lower viscosity, could you not get the same action by using silica?

T. L. JOSEPH.—The chemical activity must be considered as well as the physical character of slag. If the silica were increased the slag would not be as active chemically.

A. L. FEILD.—The point in which I am interested is whether you really get a sulfide of magnesium, showing that magnesium combines with sulfur, or whether all of the sulfur is present as calcium sulfide. I have not myself determined this fact experimentally

I have not done any systematic work on the desulfurizing properties of blast-furnace slags, but if magnesia does not combine with the sulfur chemically I wonder what particular action it could have other than upon slag viscosity. It is possible to get all the changes in viscosity within the ternary system lime-alumina-silica. The percentage of lime could be left the same, for example, and the alumina and silica could be changed. If alumina does not form the sulfide, as some of us might contend, at these temperatures, what is the mechanism that causes magnesia to improve desulfurization?

T. L. JOSEPH.—If magnesia plays no part chemically in the desulfurizing action of highly basic slags, the viscosity of such slags could be reduced by increasing the silica. However, if silica were used as a thinning agent the basicity of the slag would be lowered, resulting in a sharp decrease in desulfurization. Magnesia does act as a desulfurizing agent and can be used to lower the viscosity without materially decreasing the basicity of the slag. It is not as strong a base as lime and therefore is most effective in highly basic slags, too viscous at the prevailing temperature to permit proper physical contact of slag and metal and rapid movement of calcium sulfide from reacting interfaces.

W. A. HAVEN,* Cleveland, Ohio.—I believe most blast-furnace operators will support Mr. Feild's point of view, from actual experience. I believe that if much sul-

* Vice President, Arthur G. McKee & Co.

fur must be removed most furnace operators would place more dependence on calcite than on magnesia. It happens, however, in these days when hard slag is being largely made instead of granulated slag, that it is almost essential that about 6 or 7 per cent magnesia be introduced to effect stability of the slag for concrete work. So, while these subjects are interesting from a theoretical standpoint, the fact remains that almost all furnace producers making slag for that type of work are obliged to put in about the specified amount of magnesia. I believe, however, that most furnacemen will agree with me that that is a bit of necessary evil, and that if it were just a matter of getting out sulfur they would rather have lime than magnesia.

W. E. BREWSTER.—We use calcite. It is more obtainable. Present-day operators are used to a calcite practice; I do not think anything could induce them to adopt a magnesia or dolomite practice.

W. A. HAVEN.—I think that is generally true except for commercial requirements.

T. L. JOSEPH —I know of one plant in the East that has high-sulfur coke. About 8 or 10 per cent of magnesia has always been in the slag, because with the high-sulfur coke basic slags must be used and the magnesia is necessary to get proper fluidity.

W. A. HAVEN.—What do they do with the slag when they get through?

T. L. JOSEPH —I do not know. I talked with the blast-furnace superintendent about that very thing. He said they used magnesia for sulfur control. They did it in 1919 and are still using it as far as I know.

W. A. HAVEN —I should not be surprised to find that much of the slag is disposed of in the hard form and if the furnace is run on the basic side magnesia is needed to prevent slacking.

T. L. JOSEPH.—That plant is an exception. In 1919 I visited a number of furnaces and found that the slag made in most of the other plants contained from 2 to 5 per cent magnesia.

W. E. BREWSTER.—I know that in past practice with high-sulfur coke, or high-sulfur materials of any kind, a slight increase in the magnesia in the slag created an entirely different slag composition; that is, a mineral composition. Work has already been presented before this Institute, I believe, showing that slight difference in magnesia will cause a different mineral to be formed, which creates an entirely different desulfurizing power in the slag.

W. A. HAVEN —Of course the ranges where Mr. Joseph claims better efficiency for high magnesia are far beyond the average basicity that is used in this country. As a matter of fact, if we had to use 52 or 53 per cent of lime we would often be in bad shape.

W. E. BREWSTER.—We cannot do it.

A. L. FEILD.—This matter of the physical condition of the slag in connection with road material is something that is not new to me. We know well that magnesia forms an infusible magnesium aluminate, in conditions where lime does not. That probably is why the magnesian slags stay crystalline. It is also possible—and this is offered as a suggestion—that this action of magnesia on desulfurization may be due to its very strong affinity for alumina, thereby increasing to an extent the effective percentage of lime through formation of a stable inactive molecule of magnesium aluminate.

A. C. HARRIS,* Lackawanna, N.Y.—At one point Mr Joseph mentioned the open hearth. Does he mean that this work might also apply to open-hearth slags?

T. L. JOSEPH.—I mentioned that to point out that the mechanism of gas moving metal up into the slag, providing larger surface, would apply to the open hearth, but as far as desulfurization is concerned this work does not apply to the open hearth. In the open hearth there is somewhat the same general picture, a matter of slag basicity, but there is the question of iron oxide content of the slag and in general very much poorer desulfurizing medium than in the blast furnace. A different set of relationships would have to be worked out for the open hearth. Temperature and slag basicity would be important.

C. H. HERTY, JR.,† Bethlehem, Pa.—About 12 years ago, at Lackawanna, I sampled slag from an open-hearth heat and took the iron pellets out all the way through the heat. It was extremely interesting in this connection with sulfur that at the time the heat was melted and ready for ore the metal contained about 0.60 per cent manganese. About 10 minutes after the addition of the ore the pellets contained 0.15 per cent. The bath itself contained 0.45. After the ore had completely worked out of the heat the metal bath contained 0.15, exactly what had been in the pellets 10 min. after the ore. The bath had come to the same manganese content as the droplets, but it took an hour longer to come there. It indicates that there is a question of rate on account of the surface, as Mr Joseph said.

The average open-hearth operator would be extremely distressed if he had to make his slag for something other than making steel.

W. A. HAVEN.—I doubt that he will be put in that position very soon, because we have more blast-furnace slag than the road builders know what to do with.

T. L. JOSEPH (written discussion).—After reviewing the discussion I should like to emphasize the point that the experimental data show that magnesia is not as effective as lime in removing sulfur except in highly basic slags. The range of basicity in which magnesia appears to have merit is higher than normally used. In plants that are forced to use highly basic slags because of high-sulfur coke, magnesia appears to offer advantages.

Since the meeting in February we have made two tests to determine whether magnesia will remove sulfur from metal, forming magnesium sulfide, in connection with the question raised by Mr. Hart and Mr. Feild. Two slags were made from chemically pure oxides. Slag A contained 40 per cent magnesia and 60 per cent silica; slag B contained 40 per cent calcium oxide and 60 per cent silica. Five grams of each slag was held in contact with 12 grams of high-sulfur metal (0.8 per cent) for 30 min. at 1585° C. The high temperature was selected to assure fluid slags and rapid desulfurization. At the end of the test the metal held in contact with slag A (magnesium silicate) contained 0.008 per cent sulfur, while the metal under slag B contained 0.038 per cent sulfur. These two tests do not justify any conclusion as to the relative merits of magnesia and lime as desulfurizing agents, but they do show that magnesia will remove sulfur from metal, forming magnesium sulfide.

* Metallurgist, Bethlehem Steel Co.

† Research Engineer, Bethlehem Steel Co.

Production and Preparation of Blast-furnace Flux

By P. C. HODGES*

(Chicago Meeting, October, 1935)

WHILE there is very little romance connected with the operation of a stone quarry, yet to those who have participated in the growth and development of a business that has been a pioneer in its field and that

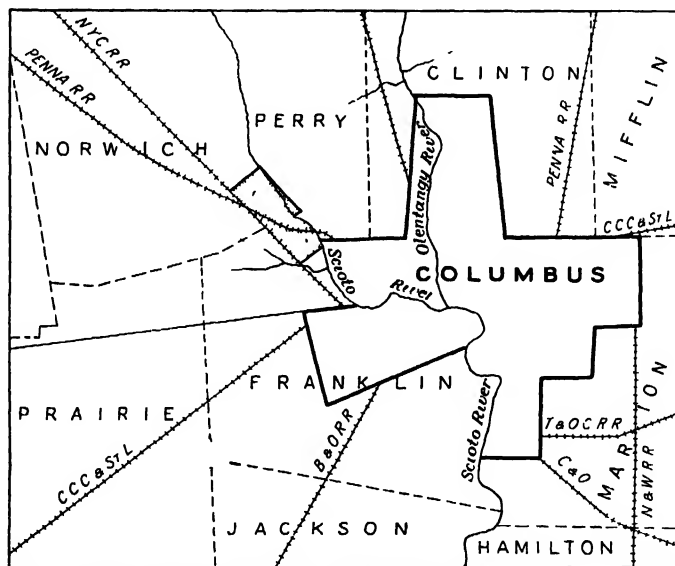


FIG. 1.—LOCATION OF PROPERTY OF MARBLE CLIFF QUARRIES COMPANY.

has been in continual operation two-thirds of a century there is bound to be a background of experience, which if properly capitalized, brings progress as well as satisfaction in its accomplishment.

The simple methods of drilling and blasting limestone and loading on to railroad cars everything that remained on a stone fork and leaving

Manuscript received at the office of the Institute Sept. 13, 1935.

* Vice President, Marble Cliff Quarries Co., Columbus, Ohio.

the rest in the quarry have now been replaced by highly technical methods of machine drilling, blasting, electric transportation, milling, beneficiation, processing and marketing, based on chemical analysis and physical tests. It is the purpose of this paper to describe the quarrying and the preparation of blast-furnace flux stone meeting certain specifications, especially as to size, cleanliness and regularity of chemical analysis; also to show that in meeting these strict requirements it has been possible, through research and the application of technical skill and equipment, for the management of a stone quarry to find uses for the byproducts of flux stone, and to develop methods for their processing.

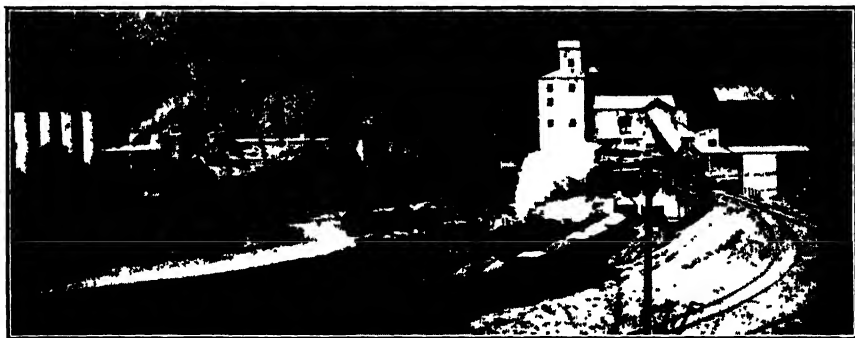


FIG. 2.—PLANTS THAT PRODUCE FLUX STONE AND ITS BYPRODUCTS.

The Marble Cliff Quarries Co., at Columbus, Ohio, is today operating the same quarry property into which the first railroad track was built in the year 1851. Even prior to that, stone for building purposes was being taken from the property in large quantities. The present company was organized in 1913, and in the following year effected the consolidation of four separate companies operating in the Marble Cliff district at that time. There are now 26 miles of standard-gage railroad tracks in the quarry.

QUARRY PROPERTY

The quarry property consists of approximately 1200 acres just five miles from the center of the city of Columbus, near the village of Marble Cliff, Ohio, and is about three miles long and one mile wide (Fig. 1.) The Pennsylvania Railroad traverses diagonally the southwest corner of the property, while the New York Central Railroad has an entrance from the west side. The Scioto River flows through the entire length of the property from north to south.

In the Geological Survey of Ohio, Series 4, *Bulletin 18*, the stone at Marble Cliff is identified as the Columbus formation, approximately

100 ft. thick and overlain by the Delaware limestone, 16 to 35 ft. deep (Fig. 3). Both are of the Devonian system. The upper half of the Columbus limestone is a crystalline buff, grayish or bluish gray, and decidedly fossiliferous. It is fairly even bedded, the layers varying in thickness from a few inches to several feet. The stone of the upper half of the Columbus limestone has been quarried extensively for many years for use as a blast-furnace flux and chemical stone.

QUARRYING

The Marble Cliff Quarries Co., in quarrying the part of the Columbus limestone ledge that is particularly adapted for chemical and flux stone, first removes the top soil or stripping, ranging from 3 to 6 ft., then removes from 16 to 36 ft. of Delaware limestone, which lies between the stripping and the Columbus limestone.

Owing to the peculiarity of the stone formation—that is, the Delaware limestone being on top of the Columbus limestone—two separate units are employed in the crushing and screening of the two kinds of stone. The Delaware limestone is unfit for chemical use, but passes A-grade specifications for all work involving the use of aggregates as well as for railroad ballast.

Therefore it is necessary, in order to prevent any mixture of the two types of stone, to be very careful in the workings of the quarry. The Delaware, or top stone, is always worked from

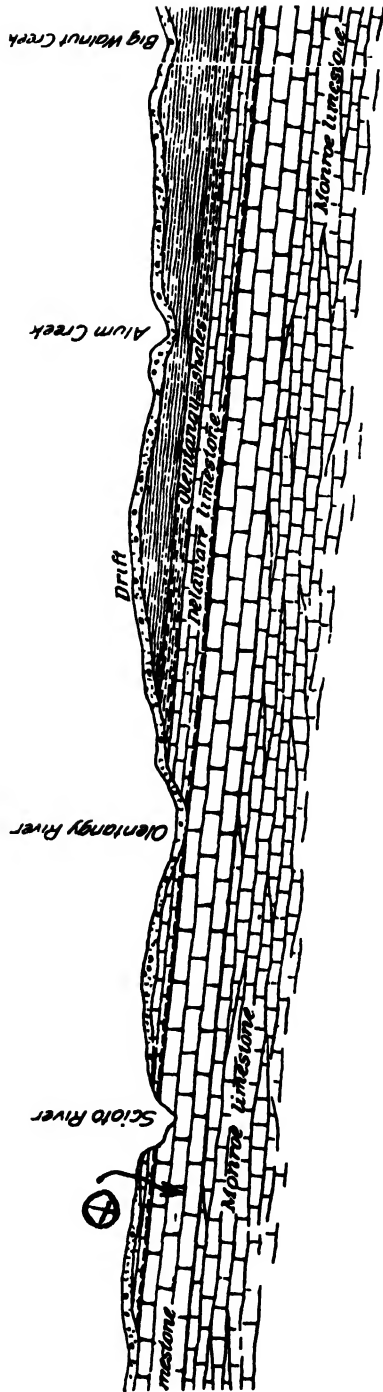


FIG. 3.—SECTION OF BEDROCK ALONG LINE DRAWN THROUGH COLUMBUS FROM WEST TO EAST.
(Portion of map from Bull 14, Ser 4, Geological Survey of Ohio.)

200 to 1000 ft. ahead of the Columbus limestone—the top surface of the Columbus limestone being regularly cleaned by air blast so as to keep the silica content as low as possible.

The top soil is loaded by shovels into standard-gage, side-dump quarry cars and hauled by steam locomotives to the dumps, located at several points in the exhausted quarries.

The Delaware limestone, after the stripping has been removed, is drilled with well drills, the $4\frac{1}{2}$ -in. holes being spaced approximately 10 ft. apart and 12 ft. back from the face. The holes are then loaded with



FIG. 4.—PORTION OF FLUX LEDGE AND WOODFORD ELECTRIC TRANSPORTATION SYSTEM. Loading simultaneously from upper, or Delaware limestone, ledge of stone and drilling farther in background.

40 to 60 per cent dynamite and shot. Railroad and tractor shovels with buckets $3\frac{1}{2}$ to 4 cu. yd. in capacity load the shot stone into 15-ton, standard-gage, side-dump quarry cars—10 to 12 cars to each train. These trains are hauled 2 miles by standard-gage, 30 to 50-ton steam locomotives, to the ballast plant, which is on the west side of the Scioto River, approximately one mile distant from the chemical-stone or flux plant.

The top portion of the Columbus limestone is now uncovered. From this top all railroad tracks are removed, after the Delaware limestone that may have accumulated along the tracks has been loaded.

Electric tractor well drills then drill $4\frac{1}{2}$ -in. holes to the bottom of the portion of the Columbus limestone that is used for chemical stone or

furnace flux. These holes are approximately 42 ft. deep. After the holes have been drilled, and before each shot is loaded, the top of the ledge is thoroughly cleaned with air. The holes are then loaded with 40 to 60 per cent dynamite and shot six holes at a time. The number of holes is limited to avoid annoyance of the neighbors. After each shot the blocks of stone that remain too large to pass through a 4-cu. yd. steam-shovel bucket are drilled with jackhammers and shot. The stone



FIG. 5.—STONE BEING DRILLED FOR POP SHOOTING, BECAUSE TOO LARGE FOR SHOVEL BUCKETS.

is then loaded by tractor steam shovels and one all-electric shovel, with 4-cu. yd. buckets, into 14-ton Woodford electric side-dump cars, which operate over the Woodford electric third-rail haulage system. They deliver the stone to the chemical-stone or flux plant, approximately $1\frac{1}{2}$ miles from the quarry.

The Woodford electric haulage system is operated by three men, in towers, one in the quarry, one about halfway to the plant, and the other overlooking the primary crusher at the plant. The operator at the plant dumps the stone from each car by electricity into the gyratory primary crusher.

CRUSHING AND SCREENING

At the crushing plant, the limestone rock is dumped from the quarry cars into a No. 21 (42-in. opening) primary crusher (No. 1 on Fig. 6), which discharges to a 42-in. incline belt conveyor (2). This conveyor delivers the crushed stone to the scalping building, and is discharged on a 72 by 168-in. Gyrex single-deck scalping screen (3) fitted with wire cloth, usually of 8-in. mesh. The size of the crushed stone that passes through this screen to the main screening plant for further sizing can be either increased or decreased, as the demand may require, by changing the mesh of the wire cloth.

The rejections that pass over the scalping screen (3) are discharged to a short 36-in. steel apron conveyor (4) which delivers the stone to a No. 10 secondary crusher (5) for recrushing. The recrushed stone is conveyed by a 30-in. incline belt conveyor (6) and discharged to the 42-in. incline belt conveyor (2) from the primary crusher and thence again over the scalping screen. The secondary crusher is set to crush to a size that will pass through the scalping screen.

The crushed stone that passes through the scalping screen (3) is fed to an inclined bucket elevator (7), 85-ft. centers, which discharges to two 48 by 102-in. Gyrex single-deck screens (8), fitted with $2\frac{3}{4}$ -in. mesh wire cloth, in the main screening plant. The minus $2\frac{3}{4}$ -in. stone that passes through these screens is discharged to a 36-in. steel apron conveyor (12), which delivers the material to the washing plant for further treatment.

The stone passing over the screens flows to two 48 by 102-in. Gyrex single-deck screens (9), which are fitted with 6-in. mesh wire cloth. The 6 to 8-in. stone traveling over these screens is spouted to a 36-in. conveyor (10) that moves slowly so that foreign material can be picked from the stone. This conveyor delivers the stone to a loading bin over the railroad track, or, in an emergency, to another 30-in. steel apron conveyor (11) traveling at a higher speed, which conveys it back to the secondary crusher for recrushing.

The $2\frac{3}{4}$ to 6-in. stone that passes through two screens (9) may be spouted directly into the loading bins, or over two 48 by 102-in. Gyrex single-deck screens (18) fitted with 4-in. mesh wire cloth for further separation.

The 4 to 6-in. stone that passes over the screens (18) may be spouted to the loading bins or to a 30-in. belt conveyor (20) and mixed with other sizes of stone. The $2\frac{3}{4}$ to 4-in. stone that passes through these screens is discharged to a 30-in. steel apron conveyor (19) operating at slow speed, so that foreign matter may be removed, and then discharged into loading bins over the track. The chutes from all screens and conveyors are designed so that the different sizes of stone can be discharged

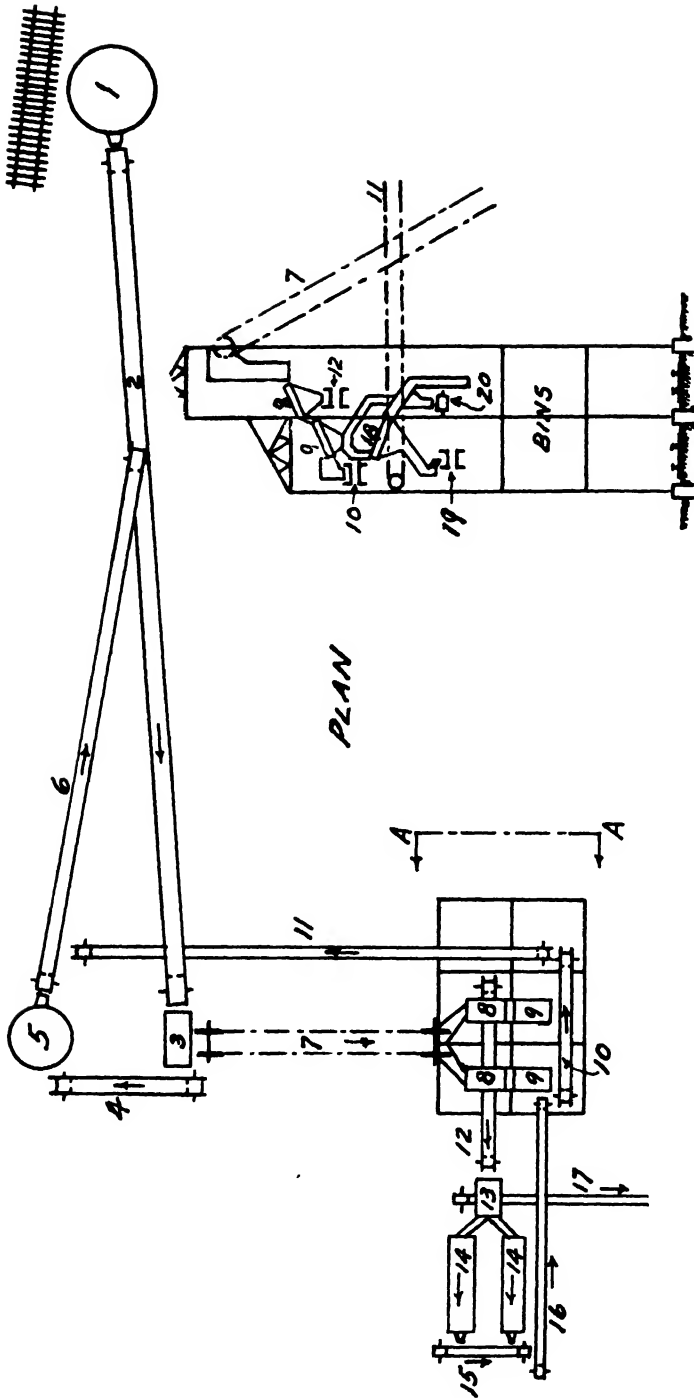


FIG. 6—MECHANICAL DETAIL OF CRUSHING, SCREENING AND WASHING.

- | | | |
|---------------------|-------------------|--------------------|
| 1. Primary crusher. | 9. Screen. | 17. Belt conveyor. |
| 2. Conveyor. | 10. Pan conveyor. | 18. Screen. |
| 3. Screen. | 11. Pan conveyor. | 19. Pan conveyor. |
| 4. Pan conveyor. | 12. Pan conveyor. | 20. Belt conveyor. |

separately or mixed with the other sizes in the six loading bins, which have a capacity of 120 tons each.

The minus $2\frac{3}{4}$ -in. stone that passes through the first set of Gyrex screens (8) at the head of the elevator in the main screening plant is delivered by a 36-in. steel pan conveyor (12) to one 48 by 102-in. Gyrex single-deck screen (13), which is fitted with $1\frac{1}{2}$ -in. mesh wire cloth.

The $1\frac{1}{2}$ to $2\frac{3}{4}$ -in. stone that passes over screen 13 is spouted to two log washers (14), 25 ft. long, which discharge the stone on to a 24-in. belt conveyor (15) running at right angles to them. This conveyor delivers the washed stone to a 24-in. incline belt conveyor (16), 57-ft. centers, which runs parallel with the log washers, and conveys the stone back to the main screening plant, where it is mixed with other sizes of flux stone as may be required.

The minus $1\frac{1}{2}$ -in. stone that passes through these screens is conveyed by 24-in. belt conveyor 17 to the main washing plant, where it is scrubbed, rinsed and screened into merchantable sizes of stone ranging from $1\frac{1}{2}$ in. down to sand.

Thus all the stone that is quarried is marketed in some form or another. The title of an article in *Rock Products* (April 2, 1927) describing the plants and processes of The Marble Cliff Quarries was "Wasteless Limestone Quarry Operations."

The plants are of approximately 5000 tons capacity each per 10-hr. day; both are electrically operated and are so similarly constructed that the ballast plant can quickly be set up to produce flux in an emergency.

UNIFORMITY AND ANALYSIS

It is obvious that all this careful beneficiation of a blast-furnace flux would be useless if the Columbus limestone were not chemically (with the right amount of magnesia) and physically fitted for use as a raw material for the blast furnace. The Columbus limestone has long been recognized as almost an ideal fluxing stone for blast-furnace use. A typical analysis of the Marble Cliff flux stone, made by the Carnegie Steel Co., is shown in Table 1. Samples are taken by the furnace operator daily from cars as they arrive at the furnace.

TABLE 1.—*Analysis of Finished Product, Marble Cliff Flux Stone*

	DRY	WET
Silica	1 76	1.74
Iron	0.20	0.20
Phosphorus	0 006	0.006
Moisture		1.10
Alumina	0.45	0 45
Lime (CaO)	50 59	50.03
Magnesia (MgO)	3 43	3.39
Carbon (CO ₂)	43 45	42 97
	99.886	99 886
Efficiency		51 23

It is recognized that a fairly uniform analysis, from day to day, is of importance to the furnace operators. A permanent record is kept of the analysis of each stratum of stone in the Marble Cliff quarries. It is, of course, well known that scarcely any two strata of stone in a given quarry will analyze the same, therefore an endeavor is made to control this situation by careful placement of shovels in different sections of the quarry and by watching closely the tonnage sent to the crushers by each shovel.

A large portion of the $1\frac{1}{2}$ -in. down screened out from the blast-furnace flux goes to the lime plant (described below) where a constant analysis is taken. If this analysis should show a wide variance from day to day, an immediate check is made of the shovels and their tonnage, to bring about a more constant mixture of the stone, thereby tending to a more uniform analysis of the flux stone as well as of the burned lime.

RATE OF CALCINATION OF MARBLE CLIFF FLUX STONE

One of the byproduct plants at the Marble Cliff quarry, which uses a considerable tonnage of the small stone, is a modern rotary-kiln lime

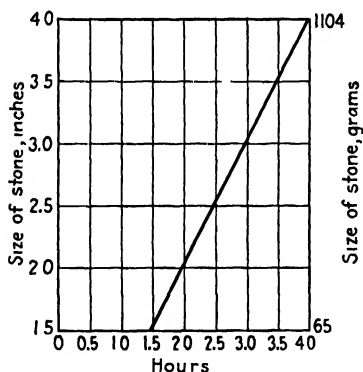


FIG. 7.

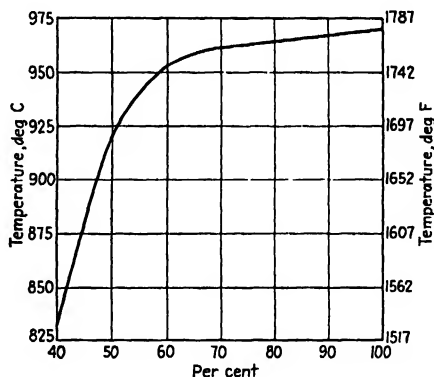


FIG. 8.

FIG. 7.—COMPLETE CALCINATION OF MARBLE CLIFF FLUX AT 970° C. (1778° F.).

FIG. 8.—RATE OF CALCINATION. CURVE DEVELOPED BY BURNING 4-INCH FLUX AT DIFFERENT TEMPERATURES UNTIL 100 PER CENT CALCINED.

plant. The continual operation of this plant since it was built has taught the company a great many things in regard to the rate of calcination of this particular stone, which should be of value to blast-furnace operators. Through the company's own experiments and through help secured from Prof. D. J. Demorest, of the Ohio State University, it has been determined that complete calcination of the standard size of flux, 4 to $1\frac{1}{2}$ in. plus, takes place within 4 hr. at a maximum temperature of 970° C. (Fig. 7). The rate of calcination is shown in Fig. 8. This has been very helpful to some flux users in the operation of their furnaces,

under $2\frac{1}{2}$ in. has worked out satisfactorily. All of our stone is brought by boat to our dock at South Chicago and is stocked in the middle of the ore dock. It is so piled as to minimize the carrying of other materials over it, thus insuring freedom from an admixture of foreign materials due to grab-bucket spillage. This, we think, is essential for we know from past experience that any stone that is mixed with ore or other materials is of uncertain quality in the proper burdening of a blast furnace.

It has always been our practice to use about 10 per cent of a good dolomite stone in our mixture to provide additional magnesia in the blast-furnace slag. Using 10 per cent dolomite in the total flux, we obtain about 4 per cent magnesia in the blast-furnace slag, and our best operation has been on furnaces from which the slag averaged just about that percentage of magnesia.

C. L. BRANSFORD, Birmingham, Ala.—We are not using limestone or dolomite on our furnace. For several years we were under the impression that we should have 6 or 7 per cent magnesia in the slags, but recently we took off all the stone and added more hard ore, and our furnace seems to be working just as well as it did with the dolomite on it. We are having no trouble.

We were using stone under 3 in., but within the next three months we will begin to size all the raw material going into the furnace. (See page 56.)

H. A. STRAIN,* Chicago, Ill.—The sizing of limestone has been given a great deal of consideration in the corporation with which I am affiliated. And it should be so: If we are to be consistent while sizing coke and removing the oversizes from ores, it is essential that we should do the same with stone. The question posed is not only one of size, however, there is introduced the relationship between size and reduction rate, which is in itself a problem. In the past we have used stone minus 5 and plus $1\frac{1}{2}$; at present we are experimenting with a stone that will range between 2 and 3 inches.

T. L. JOSEPH,† Minneapolis, Minn.—I think there are differences in the rate of calcination of stone, and I do not believe those differences have ever been very well worked out; also, the size to which a stone should be crushed may properly be varied with the rate of calcination of the stone. One thing that should be kept in mind in considering the size of the stone is the fact that the stone, being coarser than the ore and perhaps coarser than the coke, tends to roll to the more open portions of the furnace. I believe that is one of the objections against fine stone, as it gets into the more dense sections of the furnace where it is subject to less temperature and consequently reaches the lower part of the furnace and there calcines. The coarser sizes tend to roll to more open sections of the furnace and therefore have a better chance to be calcined.

R. H. SWEETSER,‡ New York, N. Y.—The tests mentioned by Mr. Hodges as convincing his company of the necessity of furnishing cleaner and smaller sized blast-furnace flux were made by me in 1909, while I was superintendent of the Columbus Iron & Steel Co. The old record in my notebook is entitled "Sweetser's Statement Showing Superiority of Small Stone." The test lasted 31 days, alternating between "big" run-of-quarry stone from the Franklin quarry, formerly owned and operated by the Columbus Iron & Steel Co., and "small" stone from the Casparis quarry, now owned by the Marble Cliff Quarries Co. Part of the time the furnace was on foundry iron and the remainder on malleable.

* Assistant General Superintendent, Carnegie-Illinois Steel Corporation.

† Supervising Engineer, North Central Experiment Station, U. S. Bureau of Mines,

‡ Consulting Engineer, Blast-furnace Practice.

The advantages of the small stone were very pronounced; there was an increase of 11.17 per cent in the weight of ore burden carried, and a decrease of 13.35 per cent in the coke per ton of pig iron. There was also a decrease of 8.44 per cent in the pounds of limestone per ton of malleable pig iron when using the small stone, and an increase of 20 tons pig iron per day, or 7.0 per cent in output.

The late Col. John Gordon Battelle, the president of the Columbus Iron & Steel Co., said that I had put their quarry out of business, but he made a satisfactory arrangement with the larger limestone company, which spent the money necessary for the proper equipment. This showed the wisdom of the man in whose memory The Battelle Memorial Institute was founded. The blast-furnace company wanted clean and properly prepared flux stone—*not* a quarry.

This paper by Mr. Hodges is the first that has been presented to A.I.M.E. on the beneficiation of blast-furnace flux. In volume 80 of the TRANSACTIONS, 1928 (the first Iron and Steel volume) there is a paper entitled, "Utilization Problems of Metallurgical Limestone and Dolomite," by Oliver Bowles. The author says, "The literature of metallurgy is notably lacking in comprehensive discussions of fluxing or furnace stone . . . the writer has made a wide review of metallurgical literature, and has had the disappointment of finding not more than a paragraph or two for each two or three thousand pages of literature reviewed."

Carbon in Pig Iron

A STUDY OF INCREASED CARBON CONTENT IN PIG IRON RELATED TO BLAST-FURNACE EFFICIENCY WITH RESPECT TO CARBON CONSUMPTION

BY WILLIAM E. BREWSTER,* MEMBER A.I.M.E.

(New York Meeting, February, 1936)

DATING back some five years ago, various foundries made inquiries as to the probable total carbon content in a given specification and grade of pig iron. Up to that time we had no data, and except for a few occasional determinations of total carbon, no attempt had ever been made to set up routine determinations of total carbon. In fact, at that time, a cast analysis was considered sufficient, without examining at further length into possible variations of analysis between ladles of the same cast.

In view of the various inquiries as to total carbon, we sampled all piles of all grades of pig iron, making complete analyses. Finding some variation in carbon content, we secured more samples and plotted the carbon content with respect to silicon in each grade of iron except for the higher phosphorus foundry iron, where it was necessary to divide the group into twenty-point phosphorus ranges. This is easily understood, owing to the falling off of carbon content with the increase in phosphorus content, silicon in each case being the same. In addition, these curves clearly demonstrate the lowering of the carbon content as the silicon is increased.

In order to insure accuracy and reliable determinations the following method of sampling and analysis was employed:

Two pigs selected from each end of the car, each car containing iron from one 50-ton ladle, are drilled with a $\frac{5}{16}$ -in. drill all the way through from top to bottom in the center of one section of the pig. The drillings are collected and transferred to an 80-mesh sieve; the portion passing through and the portion retained are placed in separate envelopes and labeled accordingly. The amount of sample in each envelope is weighed to obtain the proportionate amount of coarse and fine drillings, then a $\frac{1}{2}$ factor weight of sample (1.3636 grams) made up of proportionate

Manuscript received at the office of the Institute Feb. 17, 1936.

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amounts of coarse and fine drillings is weighed. The $\frac{1}{2}$ factor weight of sample is then mixed with a $\frac{1}{2}$ factor weight of litharge and a $\frac{1}{2}$ factor weight of low-carbon steel, on each of which a blank has been determined. The mixture is then transferred to a combustion boat and placed in the combustion furnace and allowed to remain for 15 minutes.

The CO_2 absorption bulb is weighed before sample is placed in the furnace and again after the termination of 15 minutes. The gain in weight $\times 20$ -blank = percentage of carbon.

By means of the graphs herein described we were able to answer inquiries as to total carbon content in a given grade, fairly satisfactorily and without further analyses.

With the blowing in of No. 3 furnace, a year ago—a furnace equipped with modern hot-blast stoves with ample capacity for high heats, automatic hot-blast control, automatically controlled filling, and a rotary double-screw type mud gun, capable of stopping the iron notch with no slackening of the blast whatsoever, thus making for continuous operation and blast (Table 2, column 11)—we renewed our study of carbon content in the pig iron as made by this furnace. We were prompted to do this primarily because of an apparently higher temperature of the iron as tapped, compared with our former observations of iron of like analyses on our other furnaces.

After securing 916 determinations, we again plotted the total carbon curves on various grades of iron. The malleable iron (under 0.200 phosphorus) carbon determinations shown in Fig. 1 have been selected for the comparison herein discussed. These curves were plotted against the curves previously derived from iron of our other furnaces, and we can definitely say after examining these curves that the iron made on the furnace in question (No. 3), exhibits in trend, from 10 (0.10 per cent) to 25 (0.25 per cent) points higher total carbon than had been found heretofore. (Each point plotted represents the total carbon content of the pigs poured from one 50-ton ladle.) These trends, compared with the trend of previous curves derived from other furnaces, appear in graphs shown in Fig. 1. The comparison is very marked. Both curves meet at about 0.70 per cent silicon, and become more and more divergent as we increase the silicon content. We believe that, owing to the fact that such silicon is subnormal for ordinary malleable practice, the differences in furnace operation affecting the efficiency of the fuel consumption under normal specified analyses do not exist in a subnormal and possibly badly working furnace, making 0.70 per cent silicon malleable iron.

It will be noted in Fig. 1 that carbon determinations vary considerably from the average plotted. This variance may result from three causes; (1) a discrepancy in sampling and analyses; (2) a difference in temperature at the pig machine, due to elapsed time since the iron was cast from the furnace, and (3) a variance of heat concentration in the hearth of the

furnace itself. Because of the large number of samples taken and analyzed, we do not think that the laboratory results can be questioned as to accuracy. All were made by the same personnel and in cases of extreme variation were checked and found to be correct. As to variation in temperature as poured, we have observed, in three ladles all filled at one cast, temperature drops from 2800° to 2700° F. on the first ladle poured at the pig machine and an additional 50° F. lost on each of the two succeeding ladles, making a total loss of 200° F. in temperature from cast to last of three ladles poured. This loss in temperature has been overcome

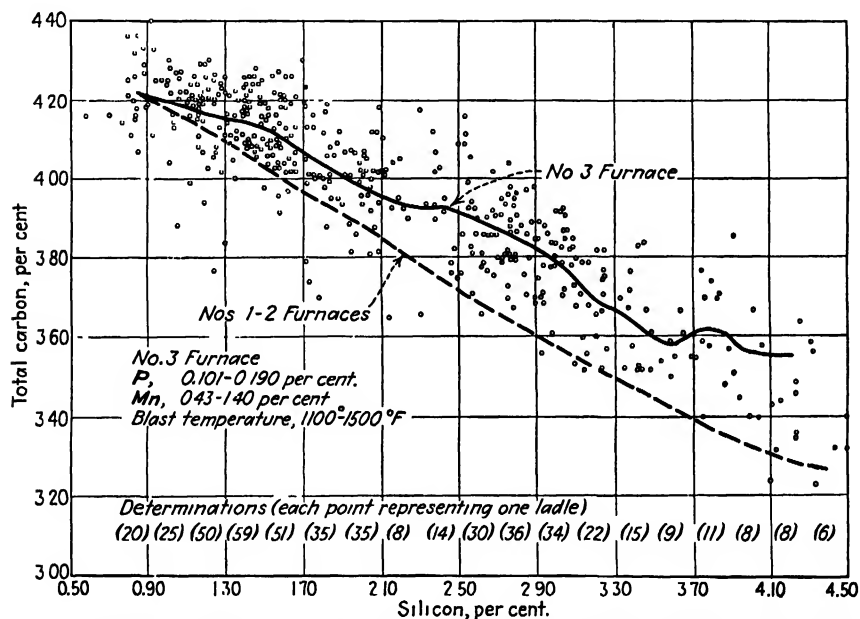


FIG. 1.—MALLEABLE IRON. COMPARISON OF CARBON CONTENT OF NO. 3 FURNACE WITH PREVIOUSLY ESTABLISHED CARBON CURVE OF FURNACES NOS. 1 AND 2.

somewhat by simultaneous pouring on two machines, and could be practically nullified through the use of a ladle of the mixer type. No doubt this difference in actual pouring temperatures is responsible for part or all of the spread in our carbon determinations.

Speaking finally of the change in the hearth condition itself, one has only to remember that the blast-furnace operators' problem is the elimination of variables. There are always some changes going on in the furnace hearth, particularly changes in the condition of the slag, which is evidenced by a change in basicity, viscosity, temperature, etc. These changes will take place regardless of the accuracy with which the charge may be figured or prepared, and no doubt have some effect upon the concentration and solution of carbon in the iron, but this effect cannot be readily determined from hour to hour, or cast to cast.

The comparison showing various phosphorus ranges is not as uniform or as regular as that of the malleable iron, and has been omitted from this discussion. An explanation of this inconsistency may be in the fact that some phosphate rock is usually charged to obtain phosphorus content in foundry pig iron. Normally it is used only to obtain the higher ranges, above 0.40 per cent, but it is quite possible that some may be used to effect quick transition from one grade to another, or where foundry ores do not provide sufficient manganese to meet the required specification. Phosphate rock is a very tricky burden constituent. It has a fusion point of 2900° F., which means that it is practically untouched in its descent through the furnace shaft until it reaches the tuyere zone, where all the action to reduce and melt it must take place. A very small amount regularly charged creates a decidedly higher coke requirement in the furnace burden. According, the heat balance in the furnace hearth itself in phosphate-rock foundry practice is seriously upset and sometimes destroyed. The writer has seen a small hearth furnace using sufficient phosphate rock to produce 0.60 per cent phosphorus in the product, go "off" from one cast to another, without any faulty movement such as hanging or slipping taking place. It is possible to drop from 3 per cent silicon to 1.25 per cent silicon with sulfur in the neighborhood of 0.100 per cent from one cast to another.

Heat is very important in determining the carbon content of pig iron, therefore we are of the opinion that the use of varying amounts of phosphate rock in our foundry mixture with a consequent variation in heat requirement is responsible for the nonuniformity of our foundry iron-carbon curves.

EFFECT OF HIGHER BLAST TEMPERATURES

Working on the theory that higher blast heats might bear a definite relation to the total carbon content, we have constructed four curves showing carbon content of malleable iron (P, 0.101 to 0.190 per cent) each on a different heat range. Unfortunately our schedules did not permit of silicon analyses covering the entire silicon range in each heat gradient, so that we do not have a similarity with respect to equal numbers of determinations between silicon percentages in each heat gradient.

In Fig. 6 are superimposed the curves of each 100° heat range to show what evidence, if any, can be detected to show that higher blast heats influenced carbon content. No evidence can be detected in these curves. This also refutes any theory that the higher carbon content of No. 3 furnace is due to higher blast heats. All of the iron made on our other furnaces was produced on blast heats under 1120° F. (Table 1, column 7).

After deriving all of these curves, therefore, we are unable to throw any more light upon the reasons for the higher carbon content of the

iron from the furnace in question. It has been very evident, particularly when making higher silicon iron and using high blast temperatures, that this particular furnace (odd numbers in Tables 1 and 2) has carried an abnormally high ore: coke ratio, and has made remarkably low coke consumption.

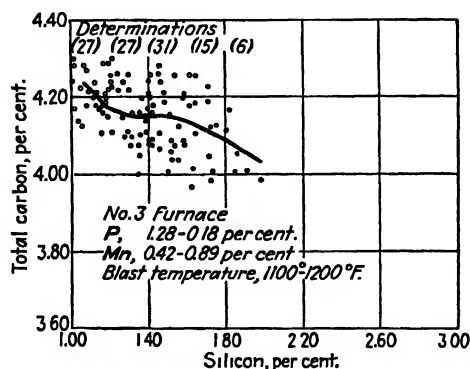


FIG. 2.—DETERMINATIONS ON No. 3 FURNACE.

Tables 1 and 2 show comparisons of this furnace (odd numbers in each case) with our other furnaces (even numbers) making similar grades of iron. Table 1 shows, taken in pairs (Nos. 3 and 4, Nos. 9 and 10, Nos. 15 and 16) that this particular furnace, on the same grade of iron, surpassed the other in low coke consumption in spite of the fact that the

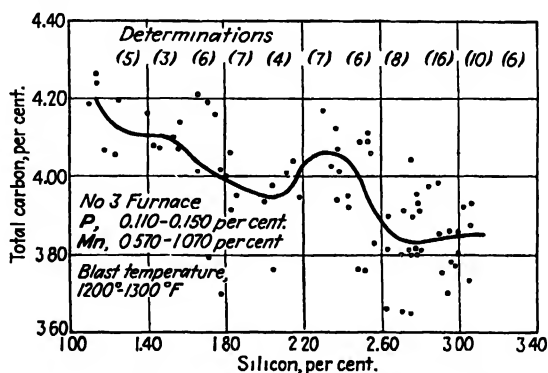


FIG. 3.—DETERMINATIONS ON No. 3 FURNACE.

other furnace used less ore per ton of iron. This led us to make calculations of carbon gasified in the furnace and reactions within the furnace to determine if possible where this increased coke efficiency was manifest, and if so, why.

All practice listed in Table 1 was accomplished on the same coal mixture, 90 per cent Benham (Kentucky) high-volatile, and 10 per cent Pocahontas. Practically identical ore mixtures and the same limestone

(Michigan calcite) were used on each furnace. No. 3 furnace is turbo-blown, other furnaces blown by reciprocating steam engines. Any variables due to burden constituents may therefore be discarded.

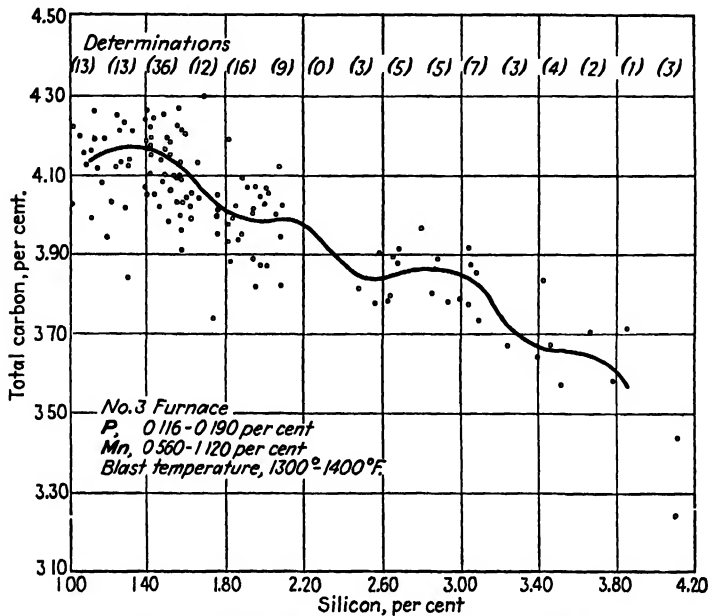


FIG. 4.—DETERMINATIONS ON No. 3 FURNACE.

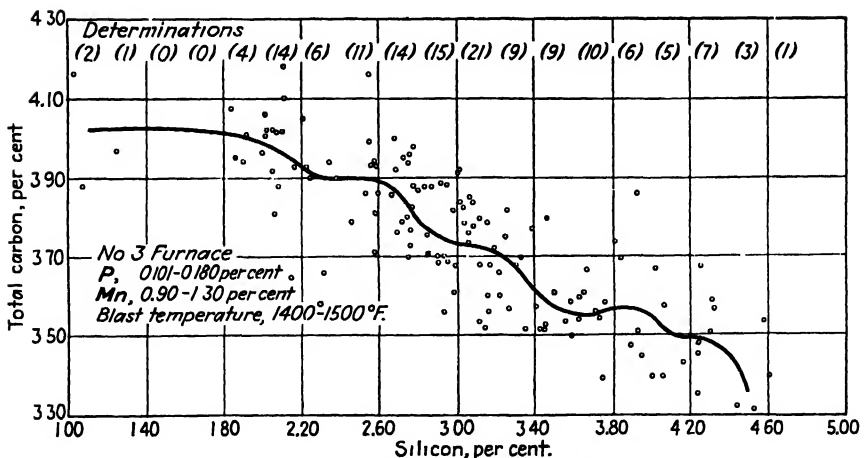


FIG. 5.—DETERMINATIONS ON No. 3 FURNACE.

CARBON GASIFIED

In Table 2, starting with the pounds of coke consumed, we correct for 1 per cent moisture and 1 per cent screenings, arriving at coke charged

TABLE 1.—*Blast-furnace Practice*

Furnace No.	(1) Tons Iron per Day	(2) Coke per Ton Iron	(3) Pounds per Ton				(4) Slag CaO + MgO SiO ₂	(5) Analyses of Pig Iron, Per Cent				(6) Average Temperature, Deg. F.		(7) Wind Blown at 62° F.	
			Ore	Re- turns	Stone	Flue Dust		Si	S	P	Mn	Blast	Top Gas	Per Min.	Per Ton
1	611	1734	4163	156	685	367	1 28	3.20	0 025	0 413	0 90	1260	375	38,620	84,300
2	621	1632	3482	400	587	205	1 18	3 19	0 031	0 243	0 89	1110	510	39,320 ^a	86,100
3	628	1650	3871	266	673	359	1 17	2 91	0 037	0 370	0 86	1270	395	37,170	84,757
4	462	1686	3241	549	614	151	1 36	2.97	0 029	0.372	0 81	1080	470	32,400 ^a	94,470
5	577	1727	4226	84	719	258	1 22	2 99	0 027	0 148	1.07	1330	350	35,880	85,600
6	439	1881	4218	69	773	312	1 39	2 87	0 028	0 159	0 98	1070	450	34,290 ^a	105,700
7	591	1694	4257	51	751	264	1 20	3 18	0 027	0 278	0 80	1320	340	35,820	83,500
8	621	1632	3482	400	587	205	1 18	3 19	0 031	0 243	0 89	1110	510	39,390 ^a	85,900
9	605	1620	4036	107	708	241	1 22	2 98	0 028	0 415	0 80	1299	340	34,820	81,400
10	466	1805	3364	464	655	51	1 29	3 11	0 031	0 430	0 72	1120	470	33,760 ^a	98,000
11	592	1644	4219	92	816	265	1 25	1 70	0 034	0 158	0 66	1171	300	34,500	82,350
12	587	1716	4576	23	792	535	1.40	1 73	0 032	0 143	0 71	1010	300	37,520 ^a	88,900
13	577	1693	4161	-7	573	236	1 21	3 22	0 034	0.165	0 82	1325	360	34,300	84,550
14	618	1629	3666	389	605	292	1 17	3 20	0 029	0 150	0 83	1100	450	39,760 ^a	87,300
15	543	1633	4114	-5	602	158	1 29	3 01	0 028	0 161	0 84	1230	290	30,140	79,600
16	466	1788	3958	101	665	205	1 36	3 13	0 030	0.161	0 82	1090	480	33,160 ^a	96,120

^a Odd numbers represent No. 3 furnace, even numbers, No. 1 and No. 2 furnaces.^b Reciprocating engines. Volume on reciprocating engines figured at 95 per cent recorded volume.

TABLE 2.—Carbon Charged and Gasified, Gas Analyses and Theoretical Wind

Furnace No.	(1) Coke per Ton Iron	(2) Tons Iron per Day	(3) Carbon Distribution			(4) Gas Analysis, Per Cent				(7) Gas per Ton Iron, Cu Ft	(8) Theo Dry Air at 62° F. per Ton Iron	(9) Carbon Gasified at Tuyers per Ton Iron	(10) Per Cent	(11) Stops on Furnace
			To Charge	To Gas	Pounds Gasified	CO ₂	CO	H ₂	N ₂					
1	1734	611	1564	1524 8	1437 9	13 4	25 8	3 6	57 2	123,300	88,900	1174	81 7	9
2	1632	621	1473	1445 6	1363 1	12 5	26 1	3 3	58 0	118,600	87,000	1148	84 3	155
3	1650	628	1488	1451 4	1362 7	13 4	24 8	3 8	58 0	119,310	86,500	1164	85 5	6
4	1696	462	1511	1496 7	1406 5	11 2	26 6	4 2	57 6	125,500	91,300	1208	85 9	137
5	1727	577	1556	1520 5	1440 8	14 3	25 2	4 7	56 2	122,600	87,000	1147	79 5	25
6	1881	439	1696	1660 3	1565 4	13 4	26 0	3 7	56 8	134,700	95,900	1265	80 8	140
7	1694	591	1527	1502 9	1411 2	14 4	25 3	3 4	56 9	120,000	86,150	1137	80 5	17
8	1632	621	1473	1445 6	1363 1	12 5	26 1	3 3	58 0	118,700	87,000	1148	84 3	155
9	1620	605	1461	1435 7	1347 5	14 7	24 8	3 3	56 4	115,100	81,165	1082	80 3	35
10	1805	466	1627	1624 9	1532 5	10 6	27 5	4 1	57 8	135,150	98,600	1303	85 0	129
11	1644	592	1482	1466 9	1366 1	15 9	23 8	3 4	56 8	117,000	84,000	1109	81 5	23
12	1716	587	1547	1489 8	1404 1	15 6	23 5	3 7	57 1	120,600	87,000	1150	81 8	165
13	1693	577	1526	1481 6	1413 0	15 3	24 1	4 4	56 2	119,000	84,600	1117	79 0	14
14	1629	618	1551	1534 1	1449 9	13 1	25 5	3 5	57 7	125,900	91,650	1210	83 5	155
15	1633	543	1472	1438 8	1366 8	16 0	23 6	3 7	56 6	115,000	82,200	1086	79 4	11
16	1788	466	1612	1584 9	1502 1	12 5	25 5	3 9	58 1	132,100	94,400	1280	85 1	135

* Odd numbers represent No. 3 furnace, even numbers, No. 1 and No. 2 furnaces

into the furnace, from which is derived, at 92 per cent fixed carbon in coke, the amount of carbon charged (column 3).

(Column 4) Carbon to gas = carbon charged + 0.12(pounds CaCO_3) - 0.04(2240) + 0.10(pounds flue dust).

(Column 5) Carbon gasified in furnace = carbon to gas - (C in CaCO_3 + C in burden).

To Determine Carbon Gasified at Tuyeres and Wind Blown

From Avogadro's law, pounds of C in 1 cu.ft. of CO, CO_2 or CH_4 are the same, may be derived:

$$28 \text{ oz. CO} = 22.4 \text{ cu.ft. at } 32^\circ \text{ F. and 760 mm.}$$

$$1 \text{ cu.ft. CO} = \frac{28}{22.4} \text{ oz. at } 32^\circ \text{ F.} = 1.25 \text{ oz.}$$

$$\begin{aligned} \text{Weight of C in pounds in 1 cu.ft. carbon gas at } 62^\circ \text{ F.} &= \frac{12}{28} \times \frac{1.25}{16} \times \\ &\frac{491}{521} = 0.031552 \text{ lb.} \end{aligned}$$

1 lb. carbon going to gas will make $\frac{1}{0.031552}$ cu.ft. or 31.69 cu.ft. of carbon gas at 62° .

(Columns 6 and 7) Taking gas analyses (monthly average obtained through daily samples), adding carbon gas percentage by volume, and dividing into pounds of carbon to gas (column 4) gives the cubic feet of gas per ton of iron:

$$\frac{\text{Carbon to gas}}{(\text{CO}_2 + \text{CO})} \times 31.69 = \text{cu. ft. gas per ton iron at } 62^\circ \text{ F. (col. 7)}$$

To determine wind blown at 62° F. :

$$\frac{\text{Cu. ft. gas per ton at } 62^\circ \text{ F.} \times \text{per cent N}_2}{0.792 \text{ (per cent N}_2 \text{ in air by volume)}} = \text{actual air per ton at } 62^\circ \text{ F.}$$

To determine carbon gasified at tuyeres:

$$1 \text{ cu. ft. air at } 32^\circ = 1.293 \text{ oz. (Richards, Metallurgical Calculations, vol. 1)}$$

$$1 \text{ cu. ft. air at } 62^\circ = \frac{491}{521} \times 1.293 \text{ oz.}$$

$$1 \text{ cu. ft. air at } 62^\circ = \frac{491}{521} \times \frac{1.293}{16} \text{ lb.} = 0.0762 \text{ lb.}$$

Air = 23.1 per cent O_2 by weight.

$$0.0762 \times 0.231 = 0.0176022 \text{ lb. O}_2 \text{ in 1 lb. of air at } 62^\circ \text{ F.}$$

(16) O_2 requires (12) C to form CO.

$$0.0176022 \times \frac{12}{16} = 0.0132 \text{ lb. C burned to CO by 1 cu. ft. air at } 62^\circ.$$

TABLE 3.—Pounds Carbon Required for Indirect Reduction of Iron in Ore

Furnace No.²	(1) Fe in Pig. Per Cent	(2) Fe in Pig. Lb.	(3) Fe in Returns, Lb.	(4) Net Fe from Ore, Lb.	(5) Carbon Gasified (col. 5, Table 2), Lb.	(6) C Required Direct Reduction, P. Mn, Si, Lb.	(7) C Available after Reduction, P. Mn, Si, Lb.	(8) C Burned at Tuyeres, Lb.	(9) C Required Ind. Red. Fe, Lb. (col. 4)	(10) C ± for 100 Per Cent Ind. Reduction (col. 8-9), Lb.	
										Plus	Minus
1	91.96	2,060	133	1,927	1,438	76	1,362	1,174	1,243	48	69
2	92.19	2,065	360	1,705	1,363	72	1,291	1,148	1,100		
3	92.22	2,066	240	1,826	1,363	69	1,294	1,164	1,178		14
4	92.33	2,068	495	1,573	1,407	70	1,337	1,208	1,015	193	
5	92.01	2,061	71	1,990	1,441	70	1,371	1,147	1,285		138
6	92.36	2,069	59	2,010	1,565	65	1,500	1,265	1,297		32
7	92.19	2,065	43	2,022	1,411	72	1,339	1,137	1,305	48	168
8	92.20	2,065	360	1,705	1,363	72	1,291	1,148	1,100		
9	92.08	2,063	92	1,971	1,348	71	1,277	1,082	1,272	240	190
10	92.21	2,066	418	1,648	1,533	74	1,459	1,303	1,063		
11	93.35	2,091	78	2,013	1,366	40	1,326	1,109	1,300		191
12	93.43	2,093	20	2,073	1,404	41	1,363	1,150	1,338		188
13	92.03	2,061	-6	2,067	1,413	71	1,342	1,117	1,333		216
14	92.20	2,065	350	1,715	1,450	70	1,380	1,210	1,106	104	
15	92.16	2,064	-4	2,068	1,367	67	1,300	1,086	1,335		249
16	92.26	2,067	86	1,981	1,502	69	1,433	1,280	1,278	2	

* Odd numbers denote No. 3 furnace, even numbers, No. 1 and No. 2 furnaces.

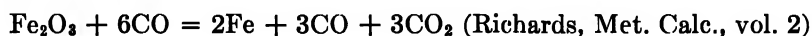
Therefore: Cubic feet air per ton (col. 8) \times 0.0132 = pounds carbon gasified at tuyeres.

It will be noted that in each pair of furnaces, No. 3 furnace (the odd numbers) gasifies a smaller percentage of carbon at the tuyeres than the other furnaces (even numbers).

Turning to Table 3, our next step is to arrive at the Fe from Fe_2O_3 , which must be reduced by CO.

We arrive at column 1, percentage of Fe in pig, from analyses of the iron: Per cent Fe in pig \times 2240 = pounds Fe in pig.

Calculating pounds Fe in returns charged (col. 3) and subtracting this from Fe in pig (col. 2) we get net Fe from ore (col. 4), which must be reduced by CO at the tuyeres. Assuming all indirect reduction, the equation being:



1 lb. Fe requires $\frac{72}{112}$ C in the above equation.

Applying this ratio to the pounds Fe from ore in column 4, we have the pounds carbon required (col. 9) for indirect reduction.

Here is where we see what is actually happening in each furnace. No. 3 furnace (odd numbers), *in each case*, gasifies less carbon at the tuyeres than is necessary to reduce the Fe from the Fe_2O_3 in the charge. In only two instances does this occur with the other furnaces. No. 3 furnace shows a deficiency in carbon gasified at the tuyeres of from 14 to 249 lb. of sufficient carbon to provide for indirect reduction of Fe from Fe_2O_3 . The remainder of the iron must therefore be reduced by direct reduction; this reaction, being endothermic in character, requires heat for its continuation, and this heat must be supplied in the form of hotter blast temperatures, which we show has been done.

Returning now to the problem of higher carbon content, with respect to No. 3 furnace, it appears that this furnace is being operated on a higher hearth temperature in order to maintain a larger amount of direct reduction. The question is still unsolved if we do not inquire as to why one furnace might carry on so much more direct reduction than another, using the same materials and not so much greater blast heat (col. 6, Table 1).

As mentioned earlier in this paper, No. 3 furnace is rarely interrupted by taking off the blast. In column 11, Table 2, we show as few as six stops on this furnace in a month's time, where the other furnaces are completely stopped from 140 to 160 times per month. Each stop causes a packing of the stock column requiring from 40 minutes to an hour's time for readjustment, during which time it is improbable that normal amounts of direct reduction may take place, particularly if the blast temperature is temporarily cut after cast to prevent hanging. We

believe that the appearance of the tuyeres in other furnaces after cast, also top and bottom pressures, generally indicate colder and irregular working during this period. When the tapping hole is stopped with no checking of the wind and full pressure is maintained, the furnace operator will notice no change in the hearth temperature as viewed from the tuyeres. He will find, however, that it becomes necessary to carry a higher ore: coke ratio in his burden when operating on this continuous basis with practically no wind interruption.

We are of the opinion, therefore, that due to a higher hearth temperature, necessary because of a greater proportion of direct reduction, made possible through more continuous application of wind, the total carbon content of the iron is increased.

SUMMARY

This paper attempts to show that we have been confronted with the problem of reconciling higher total carbon content in pig iron produced on No. 3 furnace, as compared with previous determinations on our other

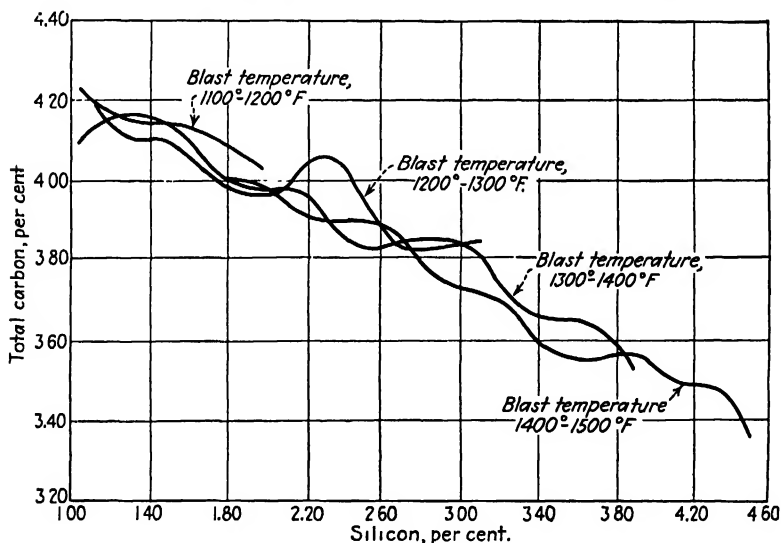


FIG. 6.—COMPARISON OF DETERMINATIONS ON NO. 3 FURNACE SHOWN IN FIGS. 2 TO 5 INCLUSIVE.

Showing effect (if any) of varying blast temperatures upon carbon content.

furnaces using the same coke, limestone and ores. There are but two outstanding differences between the operation of No. 3 furnace as compared to the others; namely, higher blast heats and more continuous application of blast.

Fig. 6 shows that a variation in blast temperature alone, varied from 1100° to 1500° F., fails to influence the total carbon content. We have shown that No. 3 furnace is consistent in gasifying less carbon at

the tuyeres than is *necessary* for the indirect reduction of Fe from Fe_2O_3 in the charge. We have, also, shown that this was not generally true in other furnace practice on lower blast temperatures and less continuous application of blast.

We conclude that direct reduction is necessary at all times in No. 3 furnace to reduce that portion of Fe from Fe_2O_3 not reduced by indirect reduction. Direct reduction *requires* approximately 1120 B.t.u. per pound of Fe reduced, compared to a *production* of approximately 1540 B.t.u. per pound of Fe reduced by the indirect method. The deficiency of heat in direct reduction must be made up by additional heat in the blast, thus concentrating more heat in the hearth, which should function toward the fixing of more carbon in the metal produced.

In the foregoing discussion and data are shown the results of our observations and analyses, and our own interpretation of them. We realize there is much more work to be done in further substantiating the ideas and data herein contained. We offer the results and our conclusions at this time in the hope that it will stimulate criticism of a constructive nature and further work, which may definitely change the present-day conception that nothing can be done in blast-furnace practice to control carbon content in pig iron.

ACKNOWLEDGMENTS

Acknowledgment of assistance is made by the author to Mr. R. A. Lindgren, Assistant Superintendent of Blast Furnaces, Wisconsin Steel Works, also to the Metallurgical and Engineering Departments for data, drawings and slides.

DISCUSSION

(*William A. Haven presiding*)

C. E. WILLIAMS,* Columbus, Ohio.—As I see it, in the No. 3 furnace, with practically the same temperature of the blast, Mr. Brewster gets a higher hearth temperature. At the same time he gets more direct reduction, and iron made by direct reduction requires more heat than that made by indirect reduction. Therefore, he gets more heat into his hearth in some manner and that must be by the more continuous application of the blast.

W. E. BREWSTER.—This more continuous operation is obtained through the use of a clay gun, which will stop the iron notch without taking the wind off the furnace, and which is not used on the other furnaces.

C. E. WILLIAMS.—It would seem that the answer is to use that kind of gun.

W. E. BREWSTER.—That, plus the fact that, of course, you have to use higher blast temperatures. I showed on the chart that, while it was not apparent in looking over the list of them, not nearly as apparent as to an operator on the job, our extremes ran from 1330 on No. 3 furnace down to 1120 on the other furnaces. There are 210°

* Director, Battelle Memorial Institute.

of variation in a maximum heat. At 210° in a blast-furnace man's understanding of operation, that is a lot of heat.

C. E. WILLIAMS.—Have you made any of the high-silicon irons with an extremely high blast temperature?

W. E. BREWSTER.—1500°.

C. E. WILLIAMS.—Those do not show a higher carbon content than others made with a lower blast temperature

W. E. BREWSTER.—In the chart I showed that the line had a distinct dip upward as the higher silicons were approached. That is where we are apt to use the higher heats, so that there is a general divergence there starting at scratch from the same point where you come down to the maximum variation in the higher silicon.

C. E. WILLIAMS.—If you want to do the opposite and make an extremely low-carbon iron you could do that by running the furnace more discontinuously?

W. E. BREWSTER.—My answer to that would be this—and I knew that question was going to come up—that the average operator that wants a low-carbon iron is not talking of merely 25 or 30 points of carbon. The operator that wants much lower carbons is the malleable operator. He would like to have it down between 2 and 3 per cent, possibly 2.25.

C. E. WILLIAMS.—Is there a demand for higher carbon irons?

W. E. BREWSTER.—The demand has been increasing, as you might surmise from the statements made, in the last two or three years; there has been a move on the part of some manufacturers of gray iron to get higher total carbon in the pig iron. I can only explain this very roughly. They tell me that although there is a carbon pickup in the cupola melting operation, carbon pickup does not produce the structure in the casting that is produced when higher total carbon is charged initially in the pig iron, arriving at the same total carbon in the casting. I think Dr. Herty probably knows exactly what I am talking about. If he can clear up that particular point it might throw a little light on this subject.

C. H. HERTY, JR.,* Bethlehem, Pa.—Very lately it has been shown that the type of carbon in the iron can be varied by varying that type of slag.

W. E. BREWSTER.—I have seen some work on that score.

W. A. HAVEN.—Is that true of total carbon?

C. H. HERTY, JR.—This did not refer to total carbon, this was on a single grade of iron where they used different types of slags. They got the carbon with the same heat and the same cooling.

In some cupola practice in which casting is continuous, suppose the blast furnace casts 15 min. instead of 4 or 5 hr., what would the carbon be?

W. E. BREWSTER.—It might be considerably lower. There is not the concentration of heat or that possibility of superheat in the hearth.

W. A. HAVEN.—That question would be difficult to answer in this country. A couple of years ago I stumbled on a little furnace in the interior of South China. It was about 8 ft. high and blown by a glorified bicycle pump driven by a coolie. The tap-hole was open constantly and casting was done by the simple means of putting a

* Research Engineer, Bethlehem Steel Co.

pole back of the furnace and tipping it over. That would certainly come in the class of furnaces that are cast frequently and make a small amount of iron.

I was curious to know what kind of iron was being produced. I brought a sample of it back with me. I can remember the carbon content, it ran 2.75 per cent. The sulfur was low. There was no sulfur to start with. They used a low-sulfur ore and charcoal.

C. E. WILLIAMS.—A number of years ago I had a brainstorm that it might be possible to make low-carbon iron by letting the iron run continuously from the hearth. Some samples of the iron taken out as it fell through the tuyere showed low carbon, about 2.75, but the sulfur was up around 0.4 per cent, as I remember it. My explanation of what happens in carbon pickup and in desulfurization was that the iron comes down into the hearth and lies there in contact with carbon and slag, where it is both desulfurized and carburized up to the point at which it comes out of the furnace. Therefore, lower sulfur and higher carbon contents can be expected if the periods between taps are increased.

I asked the question about the use of these high-carbon irons in foundry practice because a number of years ago I had experience with comparing two types of iron in a foundry that was making a very difficult, thin casting. When made from a pig iron containing about 3.75 per cent carbon, the casting showed cracks as it was taken out of the mold, whereas when made from another pig iron of the same silicon and manganese content but with 4 per cent, or higher, carbon and with the same percentage of pig iron in the charge, the castings were free from cracks. When the percentage of the low-carbon pig iron in the burden was increased to give the same total carbon in the metallic charge, as good results were obtained. It would be interesting to compare Mr. Brewster's figures on that furnace with some others of similar type.

W. E. BREWSTER.—I emphasized one thing; the coke in each case was the same, made from the same coal mixture. I do not know whether it would be possible to compare furnaces using different kinds of coke. We felt for a long time that there was a big difference in the reactivity of coke in the blast furnace with oxygen of the blast—how quickly it is burned, and so forth, and how much heat is generated in a given amount of time; all of these things have a bearing on this problem.

First of all, comparisons must be made on certain kinds of fuel; in other words, all I am trying to say here is that with what we can see there are only two differences between these furnaces, and those differences are higher blast heat and continuous application of blast. Those differences are on the one side of the ledger; on the other side, there is the difference in carbon content. It would appear that we are able on one particular furnace to make iron of a higher carbon content. I would not attempt to say what some other furnace would do using the same equipment but different coke. That would have to be worked out with other furnaces using the same coke before any comparison could be drawn.

R. H. SWEETSER,* New York, N. Y.—What was the difference in the diameter of the hearths of No. 3 furnace and the other two furnaces?

W. E. BREWSTER.—The differences were 18.6 ft. diameter and 17 ft. diameter, respectively.

R. H. SWEETSER.—That corroborates what we found last year. About two years ago we were making a comparison of carbon in steel in making pig iron. I found that a furnace with larger hearth diameter invariably gave a higher total carbon. I asked one of the big steel companies to make a test of the carbons in their steel-making pig

* Consulting Engineer, Blast-furnace Practice.

irons. It was all basic pig iron and regardless of the silicon and sulfur the hearth diameter of only $1\frac{1}{2}$ ft. greater than the other furnace invariably gave higher total carbon.

When we made the test at the Ashland No. 1 blast furnace some years ago, which was reported in our Round Table on Carbon and Pig Iron several years ago, we put that furnace on a "cold" limy slag, like that mentioned by Mr. Joseph this afternoon, and that furnace got so cold that the silicon went down to less than 0.15 per cent. But, the total carbon in that pig iron when it was all white was almost identical with the total carbon when we got a gray pig iron. We attributed the steadiness of the carbon in that furnace—of course, there was no change in the diameter of the hearth—to the kind of coke that was used.

I think, as was brought out in the papers that we had in Chicago last October, the particular coke has something to do with the total carbon in the pig iron, providing the other conditions are the same.

When there is the same coke in a furnace at $17\frac{1}{2}$ ft. in diameter and in the furnace $18\frac{1}{2}$ ft. in diameter, it is probable that if there is any variation in the carbon it is due to a difference in the diameter of the hearth. That may have something to do with the time that that metal is in contact with the column of coke or a greater surface contact between the carbon and the pig iron.

W. A. HAVEN.—I believe that conclusion might be more strongly justified if it were not for the fact that Mr. Brewster's figures show that the wind blown was really less on the smaller hearth furnace than it was on the larger one, is that right?

W. E. BREWSTER.—Almost the same. The wind per ton of iron is less on the larger hearth furnace.

C. HART, Media, Pa.—Are there more than the two kinds of carbon; the combined carbon and the graphitic carbon? I have had a great many talks with a metallurgist for one of the big iron-consuming companies in the East and he has already promised me all the pig-iron business I want if I can make a pig iron around 3.5 per cent carbon. I am not able to do it.

As I remember the furnaces about 1892, the hearth was about the same size as the top of the furnace. The boshes were so high that the furnace could be turned upside down and blown just about as well. That was the shame of those furnaces. Although we paid no attention then to carbons, I had the suspicion that those irons were lower in carbon than those we are making now. I asked Mr. Murray whether he remembered any carbon analysis and I think he said he never made any. It was not as great a factor in those days as it is now. But, I think there is something to the fact that those hearths were relatively small and the bosh was very high; it had something to do with our low-carbon operations in those days. I have a well defined recollection that we used to talk about carbon in pig iron as being 3.5 per cent.

C. B. MURRAY,* Cleveland, Ohio.—It is very seldom that we have carbon up above 4 per cent.

W. E. BREWSTER.—With what silicon?

C. B. MURRAY.—One or one and a half, basic.

MEMBER —Is there something about the combination of pig iron itself that makes it dissolve sometimes more than others? It seems to me that the first kind of carbon talked about was kish. When the iron cooled down from the temperature from which it was made it threw the carbon out and it floated on top

* Crowell & Murray, Inc.

I do not see how or why iron that is going to throw iron out of solution to such an extent can be made to take up more and have perhaps 0.5 per cent more of carbon at one time than at another.

It seems to me that the irons I have known have had a tendency, during cooling off to the freezing point, to discard carbon in the form of kish, which would float on top and come down to a given composition, making no difference what they had been when they were made.

C. H. HERTY, JR.—In that case the iron as it came from the furnace was saturated with carbon. As it cooled, it lost carbon and came out of solution and came to the top. The difference in hearth temperature and in composition, for example, in silicon and manganese alone would tend to vary the amount of carbon soluble.

I have always felt that in the blast furnace it is a question of three things: (1) What the solubility is that is effected by silicon and manganese; (2) what the solubility is that is effected by temperature; and (3) whether or not solubility is reached. It is more probable that when different cokes are being used the rate of solution is faster in one than in the other. In one case solubility would be reached, in the second it would not.

W. A. HAVEN.—Given the same conditions as far as raw materials and coke quality are concerned, Mr. Brewster has established a higher absorption of carbon for one furnace than for the other one operating under slightly different conditions.

C. H. HERTY, JR.—I was thinking that there might be more "degree-minutes" with the continuous operation.

W. E. BREWSTER.—That is it exactly.

C. H. HERTY, JR.—Mr. Brewster got the figures for the total degree minutes between casts. It might be higher on the No. 3 furnace than on the other. Therefore, it accounts for a little extra carbon.

W. E. BREWSTER.—The word "cast" in this case denotes only the taking off of the iron. It denotes no change in the furnace column.

C. H. HERTY, JR.—That is what I mean.

W. E. BREWSTER.—That additional time in which there is continuous contact of iron with heat and carbon going on makes a big difference in the problem. I think you have hit upon something there when you speak of carbon solution in terms of "degrees-minutes."

T. L. JOSEPH,* Minneapolis, Minn.—I agree with Dr. Herty. I think we have to go back, first of all, to find out the factors that determine the solubility of carbon in iron; second, we must consider whether carbon is forced down into the iron bath at all times. My conception of a furnace is that there are times when the upward pressure of the blast has a greater lifting effect upon the column than at other times and it is possible that at certain times the central part of the furnace, the so-called idle zone, is not forced down into the iron bath. Coke may be forced into the slag, but it is a question of whether the weight of the burden is enough to force the column down into the iron so that carbon is available for solution. This condition would be related to blast pressure. Slightly less wind would be blown to burn the same amount of carbon.

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W. E. BREWSTER.—That is true and the fact is borne out by the data presented.

T. L. JOSEPH.—That means there is a little less air going to No. 3 furnace, which would tend to give slightly lower pressures. There may be some tie-up between the availability of carbon and carbon in the iron.

C. H. HERTY, JR.—It is the square inch of coke surface in contact with the iron that would influence the rate.

W. E. BREWSTER.—It is quite a common thing to test the character of the stock column inside the furnace with a long poking rod inserted through the tuyeres. We have done that frequently. Very seldom, if ever, is it possible to run a rod clear through the furnace. To get it more than about two-thirds of the way is to do well

C. H. HERTY, JR.—I think Mr. Joseph was talking about the coke down in the liquid itself.

T. L. JOSEPH.—Yes. I referred to the iron collected in the crucible. Suppose there is an iron bath on the bottom of the crucible with a layer of slag above the iron. A comparatively dense inactive zone, composed of coke, partially fused slag and unreduced ore, occurs in the central area at the tuyere level and extends some distance above the tuyeres in the bosh. We are not certain that the effective weight of the stock is always sufficient to force coke through the slag layer and down into the iron.

The only way to get a starting point is to go back to what determines the solubility of carbon in iron. Moreover, is carbon always available to the same degree for solution by the iron? The time factor, as Dr. Herty pointed out, is important. I am not certain, however, that this coke is always forced down into the iron and therefore available for solution to the same degree.

We know that when the wind on the furnace is checked, the column settles and will at times force iron out of the tap-hole just before the iron notch is plugged.

W. E. BREWSTER.—It is often possible to force iron out of the tapping hole by checking the blast. In the case in question, we rarely check the furnace at all.

T. L. JOSEPH.—Not at the start of the cast, but as the iron flows checking the wind will often force out additional iron. Is the coke forced down in the iron during the operation of No. 3 to the same extent as it is on the other furnace?

W. E. BREWSTER.—That furnace is rarely checked except in fast iron runs when it becomes necessary to prevent the iron washing over with the slag.

W. A. HAVEN.—With the more continuous operation your coke ought to be higher up. Therefore you should get less carbon.

T. L. JOSEPH.—That depends on the relative importance of the short interval at cast as compared with the conditions during the longer interval between casts. The upward pressure of the blast, as opposed to the effective weight of the stock during the intervals between casts, would influence the availability of carbon for solution.

W. A. HAVEN.—Mr. Brewster has no interval at all.

T. L. JOSEPH.—Omitting the unknown effect of temperature, it is difficult to explain the higher carbon in No. 3 furnace, unless we assume that less air per pound of coke or some other factor permits the column to force coke down into the iron between casts. Carbon in the iron may be decreased by reaction with unreduced oxides in the slag. The question as to whether coke is forced down into the iron during the longer period between casts appears to be important.

W. A. HAVEN.—What is the pressure on the two furnaces?

W. E. BREWSTER.—Both about the same, or around 15 pounds.

MEMBER.—A furnace of larger diameter ought to give the coke a chance to all down.

W. E. BREWSTER.—I should like to make exception to the question of difference in the size of these two furnaces. Of course, on the drawing there is 1½ ft difference in the hearth diameter. I know that the figures on one of the furnaces were taken after the furnace had been in blast for some three or four years. During that time we had the furnace out. I know for a fact that the hearth was easily 1½ ft bigger than when she was blown in. No. 3 is practically a new furnace. I should say that the difference in the hearth diameters between the two furnaces can be almost forgotten. I do not believe there is much actual difference.

W. A. HAVEN.—Certainly if that contention were true, on a 28-ft. furnace you ought to get plenty of carbon.

C. H. HERTY, JR.—You can get only so much.

C. HART.—Is that not determined by the tuyere center? The furnace might burn out and have a bigger hearth, the tuyere circle is smaller in one furnace than in the other. All that happens is that there is a bigger place in which to accumulate materials, but the tuyere circle would remain the same as it was when the furnace was built.

W. E. BREWSTER.—The tuyere diameters do not change, of course.

P. E. MCKINNEY,* Bethlehem, Pa.—Is not much of this tied up simply with the effect of higher temperature as a result of more efficient operation, which is giving a greater temperature in the hearth? I cannot at all agree that the supersaturation of carbon can take place only if coke gets down into the hearth of the furnace. It is my belief that the iron after it leaves the fusion zone and drops down into the hearth under the slag carries the carbon that is tapped out. I base that on some observations I have made in cupola practice, in melting straight steel scrap in a cupola.

I have repeatedly taken a charge of fairly heavy scrap, charged it into a cupola, with excess charge of coke. The metal will come out tapping continuously (not being accumulated in the bottom of the furnace) with over 3.5 per cent of carbon.

When that can be done it indicates to me that it is not necessary for iron to be in contact with coke or carbon to pick up that supersaturation. It is the degree of temperature while the coke and the iron are melting and the excess coke that may be present to effect combustion.

A. HAYES,† Middletown, Ohio.—In order that there may be some prevention of unnecessary work in the further study of this problem of Mr. Brewster's, I should like to take just a moment to suggest an answer to the question in regard to the three forms of carbon mentioned. As I remember the iron-carbon diagram, in the molten state, iron carbide becomes unstable at carbon contents corresponding to something above 4.2 per cent. Accordingly, if the system is above a certain temperature, the carbon stays in solution in a stable form. If the bath with those high percentages of carbon is cooled, a temperature is reached where the compound of carbon decomposes or the liquid phase is unstable. At that time, the iron carbide that is in solution begins to decompose and liberates carbon, which comes to the surface.

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† Director of Metallurgical Research, American Rolling Mill Co.

In regard to the forms of carbon called graphitic carbon and combined carbon, I spent a number of years in studying the factors that affect the rates of breakdown of iron carbide in malleable castings. What was found is that if the silicon content is raised, the rates at which iron carbide breaks down in the solid iron are greatly increased. In fact, if the silicon content for malleable is maintained at about 1 per cent instead of 0.70, the annealing cycle for malleable castings can be shortened from about 180 hr. to about 72 hours.

It is my opinion that the carbon in solution in the solid iron is probably in equilibrium with the iron carbide present in this solution; that the formation of graphitic iron in the pig iron is a result of the graphitization or the breakdown of iron carbide in the solid phase after solidification has taken place; and that this occurs in cast pig iron containing high silicon, but not in cast pig irons having low silicon, in the period of time that remains for graphitization to take place in the cooling of the pig.

There are a number of other factors that have a marked influence also in the rate of breakdown of the iron carbide. If the sulfur as related to the manganese is too high, sulfur stabilizes the iron carbide very greatly. In fact, malleable castings with an off ratio of manganese to sulfur will not graphitize at all. They just do not anneal, whereas if the manganese-sulfur ratio is kept within ranges near that of good malleable-iron practice, which is $Mn = 2S + 0.15$, graphitization goes on very well.

I feel there is only one carbide and that is Fe_3C . These other forms of carbon are only the result of a breakdown of that compound. In one case, it is a breakdown of the compound in the liquid phase; and in the other it is a breakdown of that compound in the solid phase.

I am generally called a "brain truster," and I am more or less proud of it. I think a "brain truster" is all right if he is directed. Mr. Brewster has left the problem open. He simply presented a problem with no suggested answer. I want to say, also, that I have no suggested answer, but I want to mention a high-brow method of studying the data that Mr. Brewster has obtained. There is a book by W. A. Shewhart, of the Bell Telephone Laboratories, entitled "Economic Control of Quality of Manufactured Product," in which the author has developed an application of modern statistical methods to the analysis of data just such as these.

I notice that in Mr. Brewster's data for the variation in carbon content of his pig iron with the silicon content, there is quite a wide spread in the points he obtained at a given silicon content. This indicates that there are a number of variables affecting the quantity of dissolved carbon.

Mr. Sweetser has suggested that the diameter of the hearth may have a very important bearing on the carbon content. Some one else has suggested, I believe it was Mr. McKinney, that the temperature might be an important factor.

I would suggest that since Mr. Brewster has a number of data in connection with the silicon content—often as many as 150 observations—an attempt be made to study the data from the standpoint of what Shewhart has called "a statistically controlled experiment." If the data are studied from that standpoint, I think there would be a good chance of isolating some of the important factors that have a bearing on the carbon content. I think it would be dangerous at this time to suggest an explanation.

W. E. BREWSTER.—I think that Dr. Hayes has made a very helpful suggestion. As I said, this was a presentation of operating data.

I do want to say that I do not think that we can minimize—and Dr. Herty brought out that point—the effect of continuous application of the blast in this furnace for 24 hr. a day. I think that has a far greater bearing on carbon concentration than anybody has ever taken into consideration.

MEMBER.—Have you ever made any basic iron on these furnaces?

W. E. BREWSTER.—Yes. I purposely left the basic iron out of this calculation because No. 3 furnace has never made it. We operate normally to make enough basic iron to take care of nine open-hearth furnaces.

W. A. HAVEN.—I am glad to note that this discussion has confirmed my idea that Mr. Brewster's paper is unusual and is valuable because it has presented an enormous number of data, many more than ordinarily are given in a technical paper.

R. H. SWEETSER.—Just one word in answer to Mr. Hart's remarks about anthracite pig iron. It is a fact that the total carbon in anthracite pig iron made here in the East was lower than in the coke pig iron that we made in the West, and whether that was due to bringing down to the tuyeres a larger amount of carbon, as brought out by Mr. Brewster, or on account of the small diameter of the hearth, or the big lumps of magnetic iron ore used, we do not know. I have tried to get some anthracite pig iron here in the East but have not been able to find any.

Qualities of Pig Iron

ROUND TABLE

RALPH H. SWEETSER (MEMBER A.I.M.E.) PRESIDING

(Chicago Meeting, October, 1935)

THE Round Table on Qualities of Pig Iron, under the auspices of the Joint Committee on Qualities of Pig Iron, which is made up of members of the American Institute of Mining and Metallurgical Engineers, the American Foundrymen's Association, the American Society for Testing Materials, the Gray Iron Institute, and the Malleable Iron Institute, was held at the Palmer House, Chicago, Ill., on Oct. 1, 1935.

PROCEEDINGS

R. H. SWEETSER,* New York, N. Y.—Seven years ago last June, in Chicago, we had a round table on qualities of pig iron¹, and at that time the foundrymen were out with their battle-axes for the blast-furnace men, and the open-hearth men were doing the same thing. After that meeting there was really a determined effort to find out about the qualities of pig iron, and great progress has been made all along the line.

This afternoon we want to have a frank discussion of the qualities of pig iron, whether it is the molten pig iron going into the steel plant, or cold pigs going to the different foundries. We ought to hear something from Dr. J. T. MacKenzie, who is chairman of the Joint Committee, and from Mr. R. E. Kennedy, the Technical Secretary of the American Foundrymen's Association.

J. T. MACKENZIE,† Birmingham, Ala.—As a result of that meeting in Chicago, there was considerable agitation in the Foundrymen's Association to develop a set of tests for pig iron. One of the difficulties was that nobody talked the same language on shrinkage, draws, live iron, dead iron, and so forth, which were the main complaints against pig iron. By request of a committee of the Foundrymen's Association, the Bureau of Standards ran a comprehensive set of tests that did develop the principles governing the optical pyrometer as applied to cast iron and pig iron. Then the Bureau went on further with the fluidity test, and developed a method for the absolute changes of volume at the freezing point.

There is one serious gap in the yardstick, which has never been developed, and that is the tendency to draws from heavy sections to light. Everyone who has worried about the differences of section, and sponginess in changes of section, realizes that the

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† Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

¹ *Proc. Amer. Foundrymen's Assn.* (1927) 35, 328.

total amount of the change of volume over the freezing range is not the answer to that problem. The Bureau has been thinking about it since then, but nothing definite has been done.

We feel that the other tests are probably too scattered to ask the Bureau to do. For instance, there are the tests on cracking of plumbing cast iron; such as cracks in the little strain grid that is the overflow in a lavatory. That is prone to cracks with certain types of iron. There is no test for the shrink that occurs at the base of the foot of a cast-iron bath tub. However, those things are tested for in the casting. I think we can say that with modern methods of production certain types of defects in the foundry itself are probably the best test we ever will have, and no other test seems so well suited.

I talked with Piwowarsky about the strain grid, or "Spannungs Gitter," as it is called, which is formed of a heavy bar in the center and two light bars on the edge connected by a yoke at each end. The cracking of the yoke is supposed to measure the shrink of the iron, due to the difference in the section. I asked Piwowarsky how they were getting along with it, and he said, with that inimitable chuckle of his, that the test was fine except that when they made strain grids they lost the castings, and vice versa, so I assumed it was a total failure. Not much is coming out of Germany on the subject.

The committee is marking time. We have been trying to get a reasonably large amount of a pig iron that produces a certain fault in the foundry, and a similar pig iron that does not produce that fault, and have a promise from the Bureau that it will test it. The Bureau could not promise to do the testing next year, but we have every assurance that it will if the committee finds two such cars of pig iron. Mr. Curran promised two lots at the last meeting, and Mr. Bransford says they are trying to get them lined up now. If we can find those pig irons, I believe the Bureau will run all the tests we have on the two lots in order to determine, if possible, the cause of the cracking of the overflow grid at the back of a lavatory.

The whole committee is on the lookout for any other such occurrence, and while several cases have been reported, usually one car is all gone, or the coke or the sand was changed, or something else was done about the same time; so that it seems very difficult to get a clear-cut case of good and bad pig iron that really can be proved to have acted that way in the foundry.

R. E. KENNEDY,* Chicago, Ill.—Following the publication of the work on tests as mentioned by Dr. MacKenzie, the Joint Committee on Pig Iron Qualities sent out a questionnaire to about 100 foundries to find out whether any of them had authentic cases of "bad" pig iron; that is, iron which, according to the usual tests indicated, would produce good castings, yet which on use produced an unusual number of defectives due to such causes as shrinks or cracks. From the replies received, about 60, it was found that 18 had met cases of "bad" pig iron, but none could produce samples for the committee to check. These cases, in the main, were reported by metallurgists who, because of their standing, are recognized as reliable. Apparently they have come across cases of defective castings that they could not explain by any of their usual tests of the pig iron.

Mr. Boegehold, who is present, is one of those reporting a case of pig iron giving defective castings because of some unexplained quality, and he may be willing to discuss his findings at this time.

A. L. BOEGEHOLD,† Detroit, Mich.—If our knowledge of pig iron has not increased very rapidly, and if one man's experience seems to contradict another's, it is probably

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† Metallurgist, General Motors Research Laboratories.

because of the many different sets of conditions surrounding the manufacture of cast iron for which the pig iron is used. The foundryman who can conduct his operations without close control, perhaps because he is not required to meet quality specifications or because the nature of the casting permits considerable variation in quality of iron without causing unsatisfactory castings, is not going to learn much about pig iron, because he can get along without knowing how variation in pig iron affects his product. The foundryman who has to meet close specifications as to quality and properties usually checks his iron frequently by one or more control tests, and if he finds variation beyond the limits he has set, he usually has available several choices of procedure to adjust the quality without concerning himself as to whether the pig iron was or was not the cause. He might change the amount of steel in the charge; he might change the amount of pig iron or scrap; he might change the amount or kind of coke, knowing how each change will affect the quality of the iron. He does not care whether the deviation from within his control limits has really been caused by pig iron or not. All he knows is that the iron has changed, and he knows what to do to compensate for that change. Under these conditions, therefore, there is not much likelihood that much will be learned about pig iron. I presume this situation is typical of the majority of foundries.

There is the foundryman, however, who is operating on such a narrow margin between bad iron on the one side or the other of his specifications that he must hold every operating condition carefully controlled. Comparatively slight irregularities in operating conditions are reflected in control tests. The manufacture of iron for conversion into malleable iron is one illustration of this kind of operation. The quality balance is maintained so that the iron is white as cast in the size of castings being made, but would be gray or mottled in castings of somewhat larger section. The closer the iron can be held to the mottling threshold without overstepping it, the more readily will the castings anneal. On the other hand, if the iron changes too far away from the mottling threshold, it becomes more difficult to anneal, and if the iron is being annealed on an annealing cycle of close to the minimum time for the iron of proper quality, the iron too far on the white side will not completely anneal.

The manufacture of individually cast piston rings is another example of a closely controlled operation. The section thickness of piston-ring castings requires that, in order to meet the hardness and other physical properties specified, the iron be held close to the borderline of mottling.

Just as white iron for malleable iron is held close to the mottling range but on the white-iron side of this range, piston-ring iron is held close to the mottling range but on the gray-iron side. Deviation toward the hard side makes the castings unmachinable, and deviation toward the gray side makes the iron unacceptable from the standpoint of property specifications. In operations like these two, it occasionally happens that adjustment of any or all factors other than pig-iron quality fails to correct a faulty condition in the iron and return to normal can be obtained only by changing the pig iron. I think we could get ample testimony that this is true in these two fields of iron melting.

Personally, I know of not only one but several occasions when this has occurred in the manufacture of malleable iron, and I have been told by a piston-ring manufacturer that it is a frequent occurrence with them.

It seems, therefore, that closely controlled operations like the ones mentioned are fairly sensitive indications of variation in pig-iron quality, and that if any pig-iron producer or group of producers is interested in making a real study of what it is in the blast-furnace operation that causes quality variations not accounted for by composition as ordinarily determined, he has a fine opportunity for such a study in cooperation with manufacturers of either malleable iron or piston rings.

N. B. CLARKE, * Hamilton, Ont.—What qualities in the pig iron do you need to make good castings, or what is it that varies in the iron?

A. L. BOEGEHOLD.—The quality in pig iron is that which permits us to get in the casting the physical properties that we want to get. I can illustrate that possibly in the manufacture of malleable iron in the cupola process. The one I am familiar with uses only 10 per cent of pig iron in the charge, and that particular iron happens to be a high-silicon pig iron containing about 10 per cent of silicon. The balance of the heat is about 35 or 40 per cent steel, and about 45 or 50 per cent sprue.

Repeatedly, we have been unable to obtain suitable quality, that is, annealability, in the malleable iron when using a certain heat of pig iron, although it was only 10 per cent of the charge. Through investigation, we have found that the size of the temper carbon spot that is formed during annealing is dependent upon some quality in the pig iron. We have been able to check that repeatedly. By using one heat of pig iron from a certain furnace we get a very large temper carbon spot in the annealed iron with considerable distance between temper carbon spots. In a photomicrograph of this structure at 100 diameters the temper carbon spots would be almost 3 in. apart, and there would be only one or two of the spots on a 3 by 4-in. print. Using a heat of pig iron from another furnace, which incidentally happens to be in the same city as the furnace that made the other pig iron, the characteristics of the iron change immediately, so that the temper carbon spots are very fine. Instead of showing two temper carbon spots in a 100-diameter photomicrograph, there will be about 100, very closely spaced. The size of the temper carbon spots indicates how fast the malleable iron will anneal. The fine, close-packed temper carbon spots cause rapid annealing, while the coarse spots retard annealing and cause incomplete annealing in the annealing cycle that is fixed for that particular iron.

N. B. CLARKE.—Is that iron of the same chemical analysis?

A. L. BOEGEHOLD.—The chemical analysis, as far as we can tell from the elements we usually look for, is the same in both cases.

N. B. CLARKE.—Does the iron look like clean iron?

A. L. BOEGEHOLD.—Yes, the iron looks clean.

N. B. CLARKE.—My point is that the pig-iron manufacturer still has nothing to shoot at. He does not know what to change.

A. L. BOEGEHOLD.—The pig-iron manufacturer must get in closer touch with this problem and investigate it from the ground up. We are going to continue our investigations to try to find some reason why these temper carbon spots are sometimes fine and sometimes coarse. The difference in size of temper carbon spots is made much more pronounced by rapidly heating a sample of the malleable iron. When we heat the iron rapidly up to 1700° F., the unsatisfactory iron develops very coarse spots. The satisfactory type develops the fine spots, just as when heated slowly up to the annealing temperature. We have just been through this work, and possibly we will explain it a little more fully in a paper within the coming year.

T. L. JOSEPH, † Minneapolis, Minn.—What is the analysis of the iron that has these temper spots?

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A. L. BOEGEHOLD.—The malleable cast iron contains about 2.75 per cent carbon, about 1.15 per cent silicon, about 0.11 per cent sulfur, 0.05 to 0.06 per cent phosphorus and 0.35 per cent manganese.

F. T. SISCO,* New York, N.Y.—Have you made any effort to correlate the gas content of your iron with the precipitation of temper carbon?

A. L. BOEGEHOLD.—No, we have not recently.

F. T. SISCO.—That might be the answer.

A. L. BOEGEHOLD.—Some time ago we published some of our experiences with high-silicon pig iron for the manufacture of malleable iron, and at that time we did have the Bureau of Standards make analyses for oxygen content and nitrogen content, but there was absolutely no connection between the difficulty we were experiencing at that time and the results of determinations for oxygen and nitrogen content.

S. EPSTEIN,† Columbus, Ohio.—Is there any difference in the structure of the white iron before malleablizing, particularly of the grain size, corresponding to the coarse and fine graphite nests after malleablizing?

A. L. BOEGEHOLD.—The white-iron structure in a given section shows absolutely no difference. Of course, the white-iron structure will vary from fine sections to heavy sections. The carbide network will be much coarser in a heavy section than in a fine section, naturally. The difference in size of carbide network in the same section size is the same for the two different kinds of pig iron.

R. F. HARRINGTON,‡ Boston, Mass.—Our method of melting by means of the air furnace masks to a great extent either the merits or the demerits of pig iron. It is very difficult for us to prove the superior qualities of charcoal iron, for example, over coke iron, or some unusually good coke iron over an inferior coke iron. I think it is entirely because the metal is melted over a long period of time and at a relatively high temperature. I think it masks the effect of any unusual quality of iron in either direction.

E. L. CLAIR,§ Toledo, Ohio.—Mr. Boegehold stated a few moments ago that he felt it was more or less up to the furnace man to get closer to his problem and find out what unknown in iron is not disclosed by analysis. I have been pointedly interested in this problem for about 10 years; first, through attendance at some meetings of the Malleable Iron Research Association, and then, of course, always for the reason that we are producers of merchant iron only. We have studied this problem in conjunction with two of the largest manufacturers of piston rings in the country, and we have studied the problem in conjunction with Mr. Schwartz, of the National Malleable and Steel Castings Co.

In the first meetings with the group from the Malleable Iron Research Association, we had the immediate problem presented to us as to just what quality there was that was inherent in pig iron, not disclosed by analysis, that affected the final casting, either gray iron or malleable. And we sat back at first and took the position, "It is your problem—you tell us what you want and we will produce it." Of course, they could not tell us and they cannot tell us today. I do not know what it is today, but I can tell you something of what we have done to try to find out what it is.

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† Metallurgist, Battelle Memorial Institute.

‡ Chemist and Metallurgist, Hunt-Spiller Manufacturing Corporation.

§ Manager, Toledo Furnace Plant, Interlake Iron Corporation.

We set up a research department in our plant, and, holding the various operating factors or materials on our furnaces constant, we varied one single important factor at a time and tried to study the differences in the product. We found out immediately that it was an immense problem, and extremely difficult to bracket. We could not arrive at any focal point that we could study definitely, but we did arrive at certain generalities and I feel quite sure that we have made some progress.

On the subject of raw materials, I do not believe that there is any doubt that there is little or no chance of improvement in the quality of the ore we get from the Lake Superior region today. It is perfectly graded and I do not know of a furnaceman that would not be willing to put it on his burden without making a check analysis at the plant. Of course, we do analyze the ore, but I do not recall any great differences between the mine analysis and the furnace analysis. If there are irregularities in size and sieve test, we are, of course, aware of them and conduct ourselves accordingly. In this particular problem under discussion, I have felt that we must discount variations in ore as holding an answer to this unknown quality.

The next material in blast-furnace operation, and the most important, is coke. It has always been difficult to set up a dependable test for coke. We started to use a type of tumbler test in 1921 and have used it continuously since that time. We have found that it gives a much more dependable measure than the human eye of the physical values of coke, and we have learned that the visual inspection of coke does not distinguish good coke from bad coke, and so on. The question of ash is principally a mathematical consideration, for if when there is high ash and a greater volume of slag the amount of carbon per ton of coke has been reduced, and so on. We do not believe there is anything in the ordinary analysis of coke that has anything to do with this unknown in iron. There is, however, something inherent in any particular coke that affects the quality of the iron directly. By that I mean that with different coals, different in their geographical origin and generally in their geological origin, there will be produced different types of coke vastly different in character, which in turn will lend a different character to the iron produced. At Toledo, if we have known and studied a particular coal in the past, we can generally tell the coke from which a particular iron was made. We know, for example, that a high-oxygen coal, geologically a young coal, will give a different result and have a different effect on the carbon distribution and formation in the iron than a normal high-quality coking coal. We know that there are certain coals that yield a coke that seems to give a much more desirable form of carbon distribution, formation and particle size in pig iron. We have not found any evidence that minor variations in furnace operation, as long as that particular coke is maintained in the charge, affect the iron quality.

Then there came the threat of the users of pig iron to specify carbon, and we have investigated at some length the possibility of controlling carbon by blast-furnace operation. In studying this problem we found, incidentally, that the literature on this subject of value to the blast-furnace man was absolutely nil, and we have had to develop practically all of the operating information that we abide by today in our own plant. We believe that there is little or no possibility of controlling carbon in the blast furnace except by artificial means or after-treatment, and that the possible improvement will come not from control of the carbon quantity but of the carbon condition. This, then, comes down to the treatment of pig iron after it leaves the blast furnace. We firmly believe today that there is nothing that can be done in the blast furnace proper and I realize that that is a rather large statement. However, our investigation in over 10 years and particularly over the last four years, indicates that with uniform and unchanging raw materials, the operation of a blast furnace is more or less fixed. You can't do very much about it in the present type of blast furnace and with the present general mode of operation. I don't care to express an opinion as to how a blast furnace would operate with oxygen enrichment and I would not say that a new type of blast furnace will not be worked out in future.

There is one phase of blast-furnace operation that is not well understood. The furnace operator may produce a high-sulfur iron and reduce the sulfur by some form of after-treatment, and the analysis of the iron that is shipped will be all right. To my mind this does not mean that the iron is a good iron, for if the condition that caused the high-sulfur iron is not corrected the product may be inferior. The analysis may be good but the iron may be bad, because the condition that produced the high-sulfur iron affected the iron in other ways than by simply raising the sulfur. I believe that in the past foundrymen had trouble from this source; that is, the iron was produced from a cast made at a time when the furnace was either going bad or coming back, and while the analysis was reasonably good the conditions in the furnace due to slipping, hanging or irregularities of one sort or another did affect that iron and the foundrymen had trouble as a result. However, this sort of irregularity is rare today, and I should think that if the furnace were operated well and uniformly, and with a coke definitely known to be good, nothing further could be done to improve the product of the blast furnace as we understand it today.

The question, therefore, to be studied was the question of what could be done to improve the iron after it left the blast furnace. We have proceeded on a premise that may be incorrect but which we believe to be correct; that is, that regardless of the fact that the pig is remelted, the condition of the carbon in the pig does to a large extent affect the condition of the carbon in the final casting. The time elapsing during the melting process in the cupola does not make possible the suppression of all conditions of carbon formation in the pig iron. We believe, and this is the basis upon which we have worked, that if we can do anything to improve the form, the particle size, the condition of the particle in the pig iron, the condition that we have established will travel through the cupola and affect the casting; for the reason that in the melting process, iron comes down in successive charges in the cupola and the great bulk of the melting is done at the top of the bed. Of course, this bed burns down and is replenished by successive coke charges, but the melting time in a large cupola is so brief that we do not believe it is enough for the carbon to change its form materially.

Now, what have we done to arrive at a better carbon condition? We tried first all the methods that have been commonly used in the past, such as agitating the iron, and holding it for periods of from $\frac{1}{2}$ to 5 hr. before pouring; we built several different kinds of cascades to mechanically agitate the iron as it flowed to the pig machine; we used various forms of skimmers, and have done practically everything that could be done mechanically to improve the product. We found, however, that while this mechanical agitation had a beneficial effect, the cooling conditions were much more effective. As a result, we changed the pig machine and, after about three years of experimenting, have changed to a section of pig that does give controlled cooling conditions. By this I mean that we can cool the iron in such a manner that we could take a 3 per cent iron and cool it so that it would have 0.10 combined carbon in it, or take the same iron and produce a combined carbon of 0.65 with the same total carbon as in the first case, by varying cooling conditions on the machine. We can vary the amount of air and water cooling. The operation of this machine has resulted in a pig iron of a very close-grained gray iron. Tests of this iron show a definite increase in tensile strength of from 10 to 30 per cent as compared to a test bar of the same dimensions cut out of an old-style pig. We are, therefore, of the opinion that with controlled cooling now possible we can change the form of carbon to a form decidedly beneficial in developing the strength of the casting. We note that it is now possible to change the flaky graphite particle to one that appears thicker and sooty and which is uniformly distributed through the section of pig iron. This new type of pig has been used in manufacture of piston rings and to a lesser extent at this time in general foundry work, and has uniformly improved their product.

Whether this is the whole story or not, we do not know. I do believe that the average merchant plant today is giving an enormous amount of study to the problem,

realizing at the same time that, while the pig iron may have an unknown quality, there is always the possibility of five or six unknowns in the foundry that would affect the final casting. In most of the cases that I have investigated, and I would say that in the last 10 years they would probably number several hundred, we have been able to correct in the foundry itself the bad condition in the casting.

We also realize that the position we are taking at Toledo and in the Interlake is controversial in a way, and we do not, of course, hold that what we are doing is the final answer to the problem. We have been able to set aside certain items in blast-furnace operation and say that, as long as we hold these conditions reasonably uniform, they do not affect the problem, and we have arrived at the state of mind I have outlined, that the only thing we are able to do is to control the cooling conditions after the iron leaves the blast furnace. We feel that we have developed something of an answer in working along that road. I should like to hear an expression of opinion as to whether we are headed the right way. We believe we have made decided progress in the microstructure of pig iron, the soundness of the pig piece, and the appearance of the pig iron. Of course, the analysis has a great deal to do with the appearance of iron, and that is not controlled by the furnace people.

We believe we have made decided progress in trying to find this unknown quality and believe it to be the condition in which the carbon, particularly the graphite, exists in the pig iron, and so far as we know today we will continue our studies at Toledo along that line until we find the answer to the problem, if there is an answer.

R. H. SWEETSER.—It is evident from what Mr. Clair has said that there is something in the fuel that is used. Those who have had experience with charcoal pig iron, anthracite, and different kinds of beehive coke and coal from different sections will realize that Mr. Clair has found scientifically that there is a definite connection between the fuel and the pig iron and the castings.

J. T. MacKENZIE.—Piwowarsky, who first propounded this graphite nucleus theory, the theory that the graphite goes through the melting processes and influences the graphitization of the melt, has abandoned the idea altogether, as shown in his latest publication. He has made some tests with very rapid melting, plunging rods of gray cast iron of various compositions into molten copper for a matter of only 8 to 12 sec., just getting a little fusion, then immediately quenching in cold water. He can find no traces of the original graphite form in that quenched outer skin, so he has come to von Keil's explanation of the personality of pig iron, that it is due to the nonmetallic inclusions (not inclusions as we see them, but what they have termed the cloud or slime, or the colloidal submicroscopic form), which by definition could never be seen. But Mr. Clair's statement that he has been able to eliminate some of the troubles in the foundry by rapidly cooling the pig iron, thus influencing the graphite form, might cause us to take a little back water on that, unless we might assume that by rapid cooling, say, from one side, we had eliminated the cooling of the top of the pig before the formation of the crystals got up to that and you might have, as in centrifugal castings, practical elimination of nonmetallics to the outer surface. Unless there is some secret about it, I should like to ask Mr. Clair if it is a fact that the pig cools from the bottom to the top progressively without forming a crust on top.

E. L. CLAIR.—I did not say rapid cooling, Dr. MacKenzie, I said controlled cooling. As a matter of fact, the average section across the new pig is cooled more slowly than the average section across the old pig. It is the shape of the section of the pig that makes the difference, and its weight. The old pig was cooled practically entirely by water. There was a definite mold chill that ran up $\frac{3}{4}$ in. and an air chill that extended down perhaps $\frac{1}{2}$ in. We have developed a pig that approximates the old sand pig, not the sow, of course, but the pig itself and it is cooled by air until the

initial set has taken place. There is no perceptible mold chill or air chill, for the pig is practically a uniform structure right across its entire section. We have only been making this pig for the last four or five months and we are not entirely sure of just what can be done with it. The pigs are perfectly uniform in size, and we can control this size within a variation of 2 or 3 lb., and this improves the melting condition in the cupola decidedly. The pig is not cooled rapidly; on the average, it is probably cooled more slowly than the old pig, but there is no chance for the inside of the pig to remain molten when the outside is cooled and contracted. It is such a small section of iron that it cools uniformly across its whole section. The pig is made in a relatively large mold, much larger for the amount of iron poured in it than was true of the old pig, and this gives an entirely different cooling condition. To exemplify what we have done in studying this cooling condition: we have used molds with thermometers placed at various distances in the side of the mold and have found that the temperature of the mold affected the cooling rate and the amount of chill very materially. I do not want anyone to carry away the impression that we are chilling iron, for we are not doing that at all. We do not get any white iron, but a uniformly gray section across the whole pig. This was not true of the old-style pig where there was a definite mold and air chill. I believe the rate of cooling across the entire section is, if anything, slower than with the old pig, and we are making in effect an air-cooled pig, at least down to the point where the iron has made its initial set.

J. T. MACKENZIE.—Of course, the theory of the silicate slime leads to exactly the same conclusions as to heredity as the graphite nucleus theory. The slime that causes the original crystals in the pig forms a similar carbon graphite formation in the casting, so on that basis there is really no difference in the conclusions to be arrived at. Probably the difference in cooling the pig by allowing these slimes to coagulate, or extruding them by a process of crystallization, could profoundly influence the quality of the remelted iron. Of course, the fact that when cooled faster or slower there would be a difference in the combined carbon of the pig iron is no mystery at all. If the high combined carbon pig, or small graphite, did give the desired property in the casting, and the coarse graphite did not, with the same rate of cooling, it would cause us to go back to the graphite idea, which seems untenable, especially in view of Mr. Boegehold's operation where the total amount of graphite in the charge is so ridiculously small. A 10 per cent pig iron probably would not have 2 per cent total carbon in it. The sprue is mostly unannealed, so that the only graphite material he would have would be the annealed scrap, which is rather small.

F. J. WALLS,* New York, N.Y.—There is one point Mr. Clair did not bring out that Dr. MacKenzie enlarged upon concerning the silicate slimes. I wonder whether he has studied the slags produced in the blast furnace. Apparently the byproduct of the blast furnace is just as important as the product. It has always been my understanding that perhaps we could control some of the characteristics that are following through into our finished products by the operation of the blast furnace with respect to slag characteristics, slag volume and analysis.

C. L. BRANSFORD,† Birmingham, Ala.—In Birmingham we are working pretty much along the same lines as Mr. Clair. I agree with him that if the raw materials are right and the furnace is operating properly, the product will be satisfactory. Along the lines of cooling the molds and other improvements that have been adopted, we are doing about the same in the South.

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† General Superintendent, Republic Steel Corporation.

We have not had a complaint as to pig-iron quality in a long period, which indicates that the customers are pretty well satisfied. In fact, we would welcome some kind of complaint on physical quality of our iron, so that Dr. MacKenzie and others in the Birmingham district could go after it with the idea of determining ways and means of improving our iron. So far, however, we have not had anything of that kind that would prompt new research action.

We have one customer that buys iron on fracture, and we have a complaint now from him that we have promised to get straightened out by working between fracture and analysis; to determine the best way to solve his problem from a fracture standpoint. In working out it may be that we will find something of importance to the ironmakers and consumers.

A. L. BOEGEHOLD.—Mr. Clair and Mr. Bransford both mentioned the fact that when the furnace was operating properly the pig-iron quality should be perfectly satisfactory. I do not see anything wrong with that statement, but possibly some of the pig iron that is finding its way into the foundries was made when the furnace was not working properly. Possibly they could tell us what are the differences in pig iron produced by a furnace not operating properly. Is it an increase in iron oxide content? Is it something we can follow up and analyze, and check by tests, so that we can find out before we use it whether it is going to give unsatisfactory results?

E. L. CLAIR.—A furnace that is working irregularly passes certain portions of the stock down into the lower part of the furnace, or the crucible, without being properly reduced. The result is a cold bottom, with an insufficient amount of carbon in the bottom to take up the slack on the job that was not done properly further up in the furnace and this generally means that there are traces of iron oxide which are improperly reduced and which remain in the iron. This condition may be bad in varying degrees. For example, a furnace may be just slightly cold and there may not be proper sulfur elimination, but the iron will be physically clean, free from oxide, and will be within 25° to 50° of the proper temperature to produce normal specifications. Going further there may be a decidedly cold furnace and it may be impossible to skim the oxide from the iron like a normal slag, because it is practically as heavy as iron. This is known as "buckshot" and will go right into the iron ladle. In this case, in all probability, the iron would be bad regardless of its analysis.

However, the furnace irregularity of today is the outside exception. We have, for example, operated for over a year at a time without ever checking a furnace for hanging and I do not think there is anything exceptional about that. Operation of the average furnace plant in the country today is so far superior to the furnace operation of 10, 15 or 20 years ago that it is not the same operation at all.

There are certain rather narrow limits of analysis and temperature that a furnaceman must observe in regard to slag. They are more or less determined by the kind of iron he is making, the type of fuel, the amount of sulfur in the fuel and the type of sulfur. I believe that if we would average the slags made on the various grades of iron across the country, keeping in mind the necessary variations due to changes in fuel, we should see that these slags are remarkably uniform. There is a certain definite volume that must be observed regarding slag volume. This may change, depending upon the rate at which the furnace is operating, for a heavier slag volume per ton of iron must be used if the furnace is operating slowly. Another way of expressing it is—there must be so much gross slag per day per furnace in order to insure good operation. The limits of analysis are also very narrow. The acid constituents may be changed slightly for one furnace as compared to another, but there is not a great deal of difference in the two slags. At Toledo we have not been able to detect any microscopic difference in pig iron made with 48 or 49 total acid in the slag and iron made with 56 or 57 total acid in the slag.

J. T. MACKENZIE.—To go back to the pig iron produced in the furnace, Mr. Joseph did some work for Dr. Herty on that. I wonder if he has not something to say.

T. L. JOSEPH.—I was not directly connected with that work, but Dr. Herty conducted some tests. They were made at the Bourns-Fuller Steel Co., in Cleveland². He found that when there was a sudden change in the silicon in the iron there was a corresponding increase in the silicates, and the swings or rapid changes in the kind of iron being produced were responsible, or seemed to be responsible, for the amount of iron silicate in the iron. His final conclusion was that the iron silicate might be a factor in the cleanliness of the steel.

Recently arrangements have been made whereby the Bureau of Mines and the Inland Steel Co. are conducting cooperative studies directed toward finding out a little more about some of the questions that have been discussed a good deal; for example, the amount of oxides in iron, the effect of the furnace operation on the oxides present, and whether the oxides in the iron have any connection with the cleanliness of the steel and the quality of steel produced.

I think the difficulty in the situation has been that there has been much discussion and comparatively little intensive work. Presumably the problem is important. The solution is going to come very slowly, and I think that much work and repeated correlations will be necessary before anything is accomplished. We have not gone far enough to make any predictions as to what will be accomplished in this work, but I think if the question of oxides is critical and the question of the temperature of the iron is critical, we will be able to gather sufficient information to get some correlation in that connection.

R. H. SWEETSER.—The effect of slag on the quality of pig iron was brought out pretty clearly in our round table seven years ago at the annual meeting in New York. At that time, I presented a paper on Carbon in Pig Iron³, and gave the results of the pig-iron analyses and the temperature of the slag and the pig iron flowing from the blast furnace. I spoke of pig iron with 4.25 and 4.50 per cent total carbon, and some of the men in the East said, "Of course, Mr. Sweetser is wrong in that, there cannot be so much carbon in pig iron." They brought out the question, along the line of what Mr. Clair said, that possibly the fuels from different parts of the country have an effect on the amount of carbon carried. On the other hand, it may be the slag volume. I think that in the South the total carbon in pig iron generally is less than the total carbon in the pig iron in the Midwest, where we use entirely byproduct coke made from West Virginia coal.

F. H. CROCKARD,* Birmingham, Ala.—We have been studying total carbon lately but have not gone very far with it. About two or three years ago, our carbon was running from around 3.90 to 4 per cent, and just last week our carbon averaged from 3.50 to 3.60, with the same furnace, the same ore and the same coke. The variation may not go back as far as the coal, except in so far as it controls the structure and physical characteristics of the coke. This morning I presented some figures showing the effect of coke ash on porosity. It may be that the variation in porosity in coke may be one of the factors that controls the total carbon in the iron. Another thing that possibly may control the carbon in the pig iron would be the use of steel scrap instead of pig iron, or cast scrap, in the burden. The steel scrap and lower total carbon would naturally tend to lower the total carbon in the iron. Of course, the question arises as to whether a steel scrap or any scrap should be charged to the furnace.

² See C. H. Herty, Jr. and J. M. Gaines, Jr.: Unreduced Oxides in Pig Iron and Their Elimination in the Basic Open-hearth Furnace. *Trans. A.I.M.E.* (1929) **84**, 179.

* Metallurgist, Republic Steel Corporation.

³ Carbon in Pig Iron *Trans. A.I.M.E.* (1927) **75**, 473.

I really came here to learn about total carbon, as that is something in which we are very much interested in connection with fracture of iron, in order to get the fracture the customers want.

E. L. CLAIR.—The difference in total carbon ties in with the silicon and phosphorus content, does it not? In our practice we can predict within a couple of points what the total carbon will be for any definite analysis of silicon and phosphorus. The formula seems to hold absolutely true in our practice. For example, we make a basic iron of approximately 4.25 total carbon. Suppose we raise the silicon to 4 per cent. This will bring about a drop of 0.90 in the total carbon. If we raise the phosphorus from 0.20 to 0.70, this will in turn decrease the total carbon 0.15, or we will have a total decrease in carbon as compared to the basic iron of 1.05 per cent. The total carbon in foundry iron of 4 per cent silicon and 0.70 phosphorus would be approximately 3.20. It seems that the increase in silicon or phosphorus of 1 per cent decreases the total carbon 0.3 per cent. This seems to hold true in our practice. I am just wondering if the drop from 3.70 to 3.90 down to 3.50 was not accompanied by a corresponding increase in silicon and phosphorus.

F. H. CROCKARD.—The first figures I mentioned were taken about 1932, when we ran a number of total carbons with varying silicons in order to find out something along the line you have just mentioned. Recently, when the question came up again, we referred to those figures and found most of them were made on between approximately 2.50 and 3 per cent silicon, which gave roughly around 3.80 to 4 per cent. We have been making more analyses lately, and find that our total carbon does not run much over 3.60 with the same silicon and phosphorus.

E. L. CLAIR.—In our practice the rule seemingly applies perfectly. Recently we made some iron of 5.50 to 5.75 silicon and, compared to our normal silicon practice, we got the drop in total carbon we expected.

F. H. CROCKARD.—The two figures I mentioned were made three years apart, and in the meantime we have done a great deal of work on crushing of ore, porosity, and the size of coke, and have greatly improved our practice. That, of course, makes the analyses not absolutely comparable.

T. L. JOSEPH.—The temperature of the iron might affect the carbon; that is, with the same silicon content where the iron is uniformly hotter, there might be a higher carbon content. The furnace operating on a high slag volume might possibly be able to meet silicon specifications and control sulfurs at slightly lower temperatures; in that way the iron might be somewhat colder and there might be some change in the total carbon.

R. H. SWEETSER.—At the Ashland furnace, several years ago, when Ralph Griffis was the metallurgist there, we made some tests with the No. 1 furnace on carbon in pig iron. The blast furnace was about to be blown out and it was turned over to us for a whole week. We found the total carbon in the pig iron, while making standard basic, from 4.25 to 4.5 per cent. We deliberately ran that furnace so cold it made nothing but white iron, and the total carbon in the white iron was just the same as it was in the gray iron. For a couple of days all the carbon in the pig iron was combined carbon. There was no graphite at all. It was all white and mottled pig iron, and we ran it to a point where it seemed as though the furnace would chill up, but the total carbon was just the same.

That comes back to the point brought up by Mr. Clair, that perhaps the fuel had something to do with it. It was the same coke all the way through, made by Mr. Bransford. We were making standard basic iron, and deliberately went over to white

iron with the same amount of total carbon. The silicon went down to about 0.10, or a little bit less.

J. JOHNSTON,* Kearny, N.J.—Is there any noticeable difference in viscosity—or if you prefer, in fluidity—between the good and the poor iron, when compared at the same temperature?

E. L. CLAIR.—Ordinarily, the higher the sulfur goes, the more fluid the iron is. We notice that poor iron is very thin and very fluid. We have not made any particular studies of the viscosity of iron, but it seems to run through a rather definite range. The iron gets heavier, that is, thicker and apparently viscous, until the silicon is about 4.50 per cent, and then apparently gets more fluid. When the silicon is very high, it is very thin and fluid again. Probably this has to do with the carbon formation in the molten iron, but we have not made any study of it.

J. JOHNSTON.—Is there any evidence that two irons of nominally identical composition differ in fluidity at a given temperature?

E. L. CLAIR.—I do not believe there is any difference in the fluidity of iron at a given temperature, provided it is of the same analysis. It is, of course, possible that there could be a variation in the form of carbon existing in two different irons of the same analysis, which would affect the fluidity.

J. T. MACKENZIE.—We might ask Mr. Boegehold whether the foundry losses from mis-runs are any higher with one iron than with another.

A. L. BOEGEHOLD.—I do not know that there is any difference in mis-runs when we change from one kind of pig iron to the other. I wonder if Dr. Johnston did not have in mind that the iron that showed the difference in results possibly might have had different oxygen content, which might have had an effect on fluidity. If the chemical compositions as ordinarily determined were exactly the same, the same fluidity would be expected, but when there is a difference in oxide content I should think there would be quite a difference in fluidity. I think the presence of the oxide would show up in greater rejections, possibly in the form of cracked castings.

S. EPSTEIN.—I should like to ask Mr. Boegehold if the iron he does not like for gray iron castings is also the same iron he does not like for malleable castings. If it is not good for ordinary castings, is it also not good for malleable castings?

This problem and the problem of normality and abnormality in steel are very similar, because both are associated with fine inclusions in the iron or in the steel. When "abnormal" steel was first discovered everybody liked the normal steel and nobody liked the abnormal steel. Then many decided they would prefer the fine-grained abnormal steel. In this case, it would seem that the formation of coarse and sparsely distributed nodules of temper carbon indicates an absence of nuclei for the formation of temper carbon. That kind of pig iron might give a finer distribution of the graphite for ordinary gray iron, hence stronger and better iron, because of the absence of nuclei, let us say. Unless these things are known and understood we cannot really say when a furnace is running "properly." The pig iron from a furnace that we think is running "properly" may be worse for a certain purpose than when the furnace is running "improperly."

We cannot know just what is proper and what is improper from the standpoint of the properties of the final product unless we understand the causes and effect of inclusions, nuclei, etc., better than we do now.

A. L. BOEGEHOLD.—I do not believe we know whether the kind of pig iron that gives bad results in malleable iron would give bad results in ordinary castings. We

* Director of Research, U. S. Steel Corporation.

have never tried that. The foundries making gray iron are not under the same roof as the foundry making malleable iron, and they do not use pig of the same silicon content.

I would expect that either kind of high-silicon pig iron that we have been discussing would be perfectly satisfactory for making the gray-iron castings, because the influence of the pig iron would not be observed. If it were, we could probably adjust for it by adjusting the charge, the amount of coke, or some such thing as that. The operation in making gray-iron castings, as I mentioned at the beginning, is not as critical from the standpoint of pig-iron quality as the operation of making white-iron castings.

R. F. HARRINGTON.—Would the iron Mr. Boeghold spoke about, carry through its ill effects in any of the other methods of making malleable, particularly the cupola method?

A. L. BOEGHOLD.—The process to which I refer is melting in the cupola and then transferring to an electric furnace and superheating there. We have not had an opportunity to try out this pig iron in any other method of making malleable iron. I would suspect that the same differences in quality would not be observed with an air furnace, where conditions of oxidation during melting are quite different, from those in the electric furnace.

R. H. SWEETSER.—Coming back to the question asked by Dr. Johnston about the viscosity or fluidity of the iron, I have seen a very high graphitic pig iron that would run out of the furnace in a very sluggish stream and the iron would not run clean. It would be very, very low in sulfur; it would be very high in graphitic carbon; and the silicon might be a basic iron or it might be a foundry iron. As Mr. Clair said, if the sulfur were higher, the iron would run in a very fluid manner.

I have seen pig iron made where there was barium oxide in the slag, seeming to give a very hot slag, and the iron and the slag would be very fluid. The separating out of the graphite in certain high-temperature irons does not require high silicon.

J. JOHNSTON.—Significant comparisons of fluidity of iron can be made only on the basis of observations made at the same temperature, for it is well known that fluidity changes very rapidly with temperature. It would be interesting to make some careful comparisons, for there is at least a possibility that two irons of like nominal composition may differ in fluidity, when observed at the same temperature, particularly if one of them should carry a dispersed phase of some sort, even if the percentage of this constituent should be very small. For it is common knowledge that the fluidity of an ordinary emulsion is very much less than that of its components separately, and that the fluidity of the medium is changed far more by the presence of even a small proportion of emulsified material than by the same proportion of a substance in solution. I see no reason why this should not apply likewise to liquid iron if a second phase should under some circumstances be dispersed through it, and believe therefore that those interested would find it worth while to ascertain whether this ever occurs in practice.

J. T. MACKENZIE.—In the Belgian exchange paper presented at the International Foundry Congress last year, there were shown some rather astonishing differences between two irons from different sources, although apparently they were the same temperature and the same analysis.

R. H. SWEETSER.—In view of what Mr. Clair has said about the smooth running of the blast furnace nowadays, probably very few of the blast-furnace men present know anything about "buckshot." Those who do, know there is a condition when the iron is very, very far from fluid, and when the viscosity is so high the iron has to be actually pushed out over the dam. That was when the furnace was so cold there was practically no separation of the slag and iron, and there would be a cold, very viscous slag with particles of iron like buckshot all through it. No foundryman ever got any pig iron from that kind of furnace, because the iron could not be cast.

R. S. MACPHERRAN,* West Allis, Wis.—Mr. Clair suggests that the presence of high sulfur is not in itself an indication of the vast difference. I have heard that a high sulfur in the pig iron is an indication that the furnaceman is making "off iron." Is that true? Does a high sulfur in itself mean an "off iron"?

E. L. CLAIR.—I presume Mr. MacPherran means that the furnace would be off as regards normal operation, and to that I would say yes. We do not try to make high-sulfur iron, and if it were produced the indication would be that the furnace was not working normally.

R. S. MACPHERRAN.—You really are making off iron, then?

E. T. CLAIR.—Yes, off-specification iron.

F. WALLS.—Dr. MacKenzie said something about shrinkage and susceptibility to cracking. Why does one carload of pig iron make pretty good castings in the foundry for a day or half a day, and the next day when another car of pig iron from the same blast furnace and same analysis is put on the burden, other things being equal, a considerable amount of shrinkage occurs? For 20 years I have been trying to answer that question for myself. I have never laid it entirely to the pig iron. I am inclined to think it may be due to atmospheric conditions, cupola operations, and so on. But we will assume that it happens on days when atmospheric conditions are practically normal; one day there is a lot of internal shrinkage in the castings, and the next day there is none. I think Dr. MacKenzie had that in mind when he spoke of susceptibility of cracking in the strainers. Is it tied up somewhat with molding practice? There have been some theories that shrinking is caused by soft ramming of the mold, that there is not enough pressure exerted during the solidification range and expansion period to push in that iron.

R. F. HARRINGTON, Boston, Mass.—A great deal of shrink can be caused by molds that are soft in one place. Often, on a cylindrical casting, we can trace the presence of shrink to the part of the mold that was softer than the portion of the mold immediately above or below it. In our own practice we have to tie up very carefully the question of mold hardness with that of internal shrinkage. That is one of the reasons we have often been unwilling to condemn the pig iron, because we have felt that we should look into our own practice before condemning the pig.

There is one thought I should like to leave with the committee investigating the question of shrinkage of pig iron; that is, if the phosphorus in the metal is lowered, I think we are all agreed that the amount of shrinkage at heavy and light sections will be reduced. On the other hand, the shrinkage is not materially changed in a perfectly cylindrical casting by the same reduction of phosphorus. So I would not like to see the entire effort on the study of shrinkage placed upon the study of K-bars or bars of that nature.

Also, I think the committee ought to consider other more simple types that may have a shrinkage caused by a somewhat different effect.

J. T. MACKENZIE.—We assume that the shrinkage in an even section would be directly proportional to the change of volume passing from liquid to solid. The Bureau of Standards method is an absolute measure of that; a beautiful method. It is the K-bar shrinkage that so far we have not been able to put a number on. We can cast a K-bar, and can say, "Yes, this has a big hole in it," and "This has a little hole," and "This has nothing to speak of," but so far we have never been able to give it a number. Until we are able to do that, I do not feel that we have a good test for what I call "draw."

The total shrinkage in an even cylinder is simply the change of volume, and that is the one that is not affected to any extent by phosphorus, whereas the draw shrinkage is affected by phosphorus, which gives a long freezing range.

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R. F. HARRINGTON.—I merely wished to point out that I think both phases of it should be investigated. Apparently the committee has that very definitely in mind.

MEMBER.—Is not the kind of steel scrap used in the cupola charge responsible for change in the quality of the malleable iron?

A. L. BOEGEHOLD.—We are pretty firmly convinced that the scrap has not the slightest thing to do with our trouble. As you say, it is steel scrap and it is bundle scrap, but it is not miscellaneous by any means, because it is carefully selected, clean, free from rust and free from terne plate or any other material that will cause trouble in the making of malleable iron. It is all deep-drawing automobile-body steel that has been bundled at one of the body plants, and is quite uniform. If everything we use in the cupola were as uniform as that scrap, we would have no trouble at all. Each time we put this one type of pig iron on the charge, we get the result I mentioned before; that is, coarse temper carbon spots after annealing. We can take off that pig iron and put on the other pig iron, and not change anything else, and we will get the other result. We can do that week after week, as long as we want to keep it up, other things remaining the same.

R. H. SWEETSER.—How is that melted; in a cupola, or in the air furnace?

A. L. BOEGEHOLD.—In the cupola.

R. H. SWEETSER.—Ordinary coke, or extra good coke?

A. L. BOEGEHOLD.—We try to keep it as good as possible. We are very fussy about the coke, because that is another important factor influencing the quality of the iron.

H. A. STRAIN,* Chicago, Ill.—I am always rather on the outside with my confreres and brethren in this blast-furnace business, but I believe we are going to have to take up this problem in more than a joking light. There have been many statements this afternoon that, to my mind, if they had been amplified, would have been along lines on which we could have approached our subject.

I agree with Mr. Clair up to a certain point, but when we say there is nothing we can do to a blast furnace to improve its product or to change it, we are covering a great deal of ground. There are slag conditions in the blast furnace that can be changed, that will change its viscosity and make it a different product. What that means physically, I do not know, nor does anybody else. This will all happen without material change in the chemical analysis.

I have had experiences with certain slags in merchant foundry irons of very low melting point that would take a great deal of heat, and have cast iron from that slag of a high-silicon grade that was very thin, and other slags of the same chemical analysis would cast very thick. I am talking now about small hearth furnaces.

When we get definitions or indices by which to follow that thought, will we not have solved the problem, or at least have a better yardstick for pig iron than we have today? We can follow along those lines much as the man in steel has had to approach them.

In my short time in the iron and steel business, I remember when steel went out of a plant on the plant's own specifications. Today the specification applied is after that same piece of steel has been processed three or four times in the customer's plant.

Is pig iron approaching the same condition? If so, it behooves each and every man producing pig iron today to get his tools out of the closet and go to work.

* Superintendent Blast Furnaces, Carnegie-Illinois Steel Corporation.

Temperature Measurements with the Disappearing-filament Optical Pyrometer

By W. E. FORSYTHE*

(Chicago Meeting, October, 1935)

DIFFERENT forms of optical pyrometers are discussed and the advantages and disadvantages of the different types for measuring high temperatures are pointed out. These advantages and disadvantages lead to the selection of the disappearing-filament type of optical pyrometer for most work. Attention is directed to the necessity for the use of a monochromatic screen with a pyrometer, which leads to a discussion of the meaning and use of the effective wave length of the screen.

Methods of calibrating the optical pyrometer are outlined and it is shown that an optical pyrometer can be calibrated just as definitely as any other temperature-measuring device. Accuracy tests are included, in which it is shown that excellent results can be obtained by even untrained or slightly trained observers with this form of optical pyrometer. The various corrections that are necessary in this kind of work are indicated, including corrections for stray light, for absorption of windows, of smoke, and so forth.

The troublesome problem of measuring the temperature of bodies that do not radiate like a black body is discussed and the corrections for reducing such readings to the true temperature are given for a number of different materials.

INTRODUCTION

The fundamental idea of temperature depends upon our temperature sense and bodies are said to be hot or cold depending upon the reaction of our hands or some other part of the body to the heat from the source investigated. For measuring the temperature some instrument must be devised, since the temperature of the source studied is apt to be so hot as to greatly injure any part of the body that comes near it, to say nothing about direct contact with it.

Definition of Temperature.—The temperature scale is based upon two fixed points, the temperature of freezing water and the temperature of boiling water. This temperature interval, depending upon the scale

Manuscript received at the office of the Institute Dec. 30, 1935.

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used, is divided into steps of different sizes, called degrees. The Centigrade scale is based upon the division of this fundamental interval into 100 parts called Centigrade degrees. One may then say that 1°C. means a temperature change that will cause $\frac{1}{100}$ of the expansion of mercury between the ice point, which is marked zero, and the boiling point, marked 100° . But at higher temperatures difficulties are encountered. Does mercury expand the same amount for 1° change in temperature at all temperatures? Further, the boiling point of mercury is relatively low. A gas expands uniformly over a wide range of temperatures, so a gas thermometer might be made and if the expansion of the real gas is corrected to that of a perfect gas, accurate values of the temperature can be obtained for as high a temperature as the container of the gas can be operated.

It was the difficulty of accurately defining a temperature interval for all temperatures that led Lord Kelvin to introduce his notion of "absolute thermodynamic scale" of temperature. This scale is based upon the amount of work obtained by the operation of a perfect engine in the well-known Carnot cycle between two sources of heat at different temperatures. The amount of work obtained can be shown to depend upon the difference between the two temperatures, which gives a measure of a temperature interval. This is the same temperature scale that would be obtained if a perfect gas could be used as the measuring substance. Neither of these methods can be used in practice, but when the black body is discussed a method of realizing this thermodynamic scale will be described.

If the temperature of the source is continually raised, a point is soon reached where no known substance will, in general, remain constant in any of its temperature-measuring properties if placed in direct contact with the source. It is also occasionally necessary to measure the temperature of a source that is so small or so situated that it would be very hard to bring the measuring instrument into direct contact with the source.

Temperature and Brightness.—Whenever the temperature of the source becomes too high to bring the measuring device into contact with it, temperatures are measured by taking advantage of the fact that all bodies, when at sufficiently high temperatures, send out radiation in amounts readily measurable.

All of the early workers of iron and other metals, and many modern workers, judge temperatures in part by the amount of light given off; that is, by its surface brightness. A blacksmith has but little idea of the measuring of temperature, still he knows when iron is hot enough for welding, forging and bending, although each requires a different temperature.

The Black Body.—A study of hot bodies has demonstrated that different radiators when heated to the same temperature give off different amounts of light. This led to the idea of a standard radiator; that is,

one that radiates according to a definite rule. Such a radiator is a black body, the standard of all radiators.

The black body has been defined by Kirchhoff as a body that will absorb all the radiation that it receives; that is, it will neither reflect nor transmit any of the incident radiation. The radiation from such a body is a function of the temperature alone. There is no known substance that has exactly this property; the nearest approach is probably some form of untreated carbon. It has been shown theoretically that a cavity with walls at a uniform temperature possesses the properties of a black body. If a small hole is made in the wall of the cavity the radiation from this hole will approximate that of a black body. The smaller the hole in proportion to the size of the cavity, and inversely in proportion to the emissivity of the material of the walls, the nearer this approximation.

Experimental Black Body.—

Many attempts have been made to realize this uniformly heated cavity with an opening through which the radiation can be studied. The one most commonly used for temperatures above 1000° K. consists of a refractory tube more or less uniformly wound with platinum ribbon and containing a central diaphragm and other diaphragms, all with small holes in them. Fig. 1 shows such a furnace with the space between the two heater tubes filled with pure aluminum oxide and with two tubes slipped inside of another tube that has been packed with a good heat-insulating material.

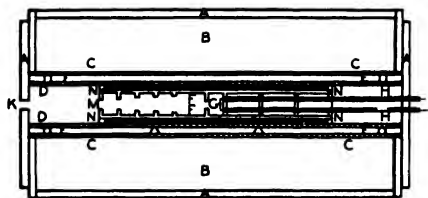


FIG. 1.—DIAGRAM OF BLACK-BODY FURNACE TUBES *F* AND *D* WOUND WITH PLATINUM RIBBON

Tube *F* is wound uniformly and tube *D* about as shown to aid in correcting for end cooling. The space between the two tubes is filled and packed with very pure aluminum oxide. To prevent sagging, tube *D* is supported at two points, as shown, by supports *O*. Space outside of tubes (*B*) filled with infusorial earth.

Black-body Laws.—The first rule found for the radiation of a black body was that the total energy radiated per unit area of the standard radiator was equal to a constant times the temperature raised to the fourth power. This, however, does not tell us how much light is given off by the body at different temperatures. Again theory showed that the relation between the energy output for any wave length depends only upon the wave length and the temperature. The equation (No. 1) that expresses this relation was developed by Planck and is referred to as Planck's radiation law:

$$J_{\lambda} = \frac{c_1 \lambda^{-5}}{e^{\frac{c_2}{\lambda T}} - 1} \quad [1]$$

For small values of the product λT , this reduces to the more simple form derived by Wien,

$$J_{\lambda} = \frac{c_1 \lambda^{-5}}{e^{\frac{c_2}{\lambda T}}} \quad [2]$$

The temperatures entering the black-body laws are all "absolute thermodynamic temperatures," since these laws were derived with this basis for the temperature interval. Thus, using the black body and basing the temperature on the brightness, either total or spectral, as given by these laws enables this temperature scale to be established.

Optical Pyrometers.—The eye is not a very reliable instrument for making absolute measurements of the intensity of light but it is very sensitive to differences in brightness between two adjacent surfaces. Thus, to secure accurate estimates by eye, a comparison source is necessary. The introduction of a comparison source is the first step toward

an optical pyrometer, which consists of a comparison source and some convenient arrangement for matching this source, either in brightness or in color, against the source studied.

Pyrometers are divided into three classes, on the basis of either the method of introducing the comparison source or the method of making the comparison between this and the source being studied.

The first class has its comparison

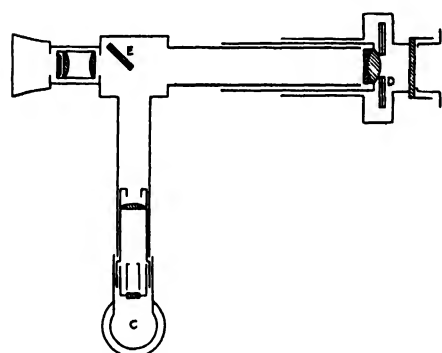


FIG. 2.—LE CHATELIER OPTICAL PYROMETER.

source arranged as shown in Fig. 2. The image of this comparison source is reflected into the eyepiece by a mirror or prism at the focus of the objective lens.

In class two, called the polarization type, an image of the source studied and that of the comparison source are observed through the same eyepiece with the light from the two sources polarized in planes at right angles to each other and the balance made by rotating a nicol in the eyepiece.

The third class, called the disappearing-filament type, has as a comparison source a lamp filament, called the pyrometer filament, which is located at the focus of the objective lens. In using the pyrometer, the hot object is seen with the pyrometer filament crossing it, so that the filament appears much the same as the cross-hairs in an ordinary telescope.

There are two types of disappearing-filament optical pyrometers. In the first, the photometric balances are made by varying the current through the pyrometer filament. In the second, the filament is kept at a constant current, and thus at a constant brightness, and balances are made by rotating a wedge-shaped circular absorbing screen between the

pyrometer lamp and the objective lens, thus varying the apparent brightness of the image of the source studied. A diagram of this pyrometer is shown in Fig. 3.

An Early Optical Pyrometer.—Some of the engineers who were connected with the early work on incandescent lamps had trouble in setting and resetting their furnaces, for treating filaments, at the proper temperature to produce the best filament for the lamps they were then making. These engineers, sometime in the early nineties, hit upon the plan of using

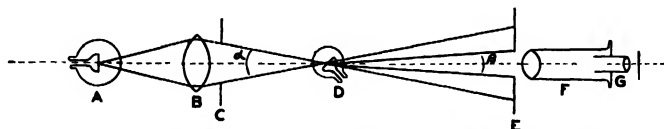


FIG. 3.—ARRANGEMENT OF DISAPPEARING-FILAMENT PYROMETER.

A, background.

D, pyrometer filament.

F, eyepiece

B, objective lens

E, eyepiece diaphragm.

G, monochromatic filter.

C, entrance cone diaphragm.

as a comparison source for this purpose a lamp operating at a certain percentage of its normal voltage and holding this lamp between the eye and the furnace, setting the furnace at such a temperature that it appeared to have the same brightness as the lamp filament. The furnace temperature was stated in terms of per cent voltage of a lamp of certain watts per candle.

Recently a new lamp has been designed¹ for this purpose, which overcomes some of the earlier difficulties. It consists of a bulb (Fig. 4) in which is mounted a sturdy, inverted U-shaped carbon filament, selected for uniformity, and a small eyelet. The filament and background to be measured are viewed through the two windows on the sides of the bulb. The black coating on the bulb reduces the glare from parts of the background in the vicinity of the area being measured. The small eyelet always appears black against the field and is an aid in keeping the eye focused on the proper part of the filament when it is about to disappear.

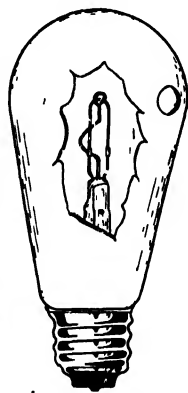


FIG. 4.—A PYROMETER LAMP WITH BULB CUT AWAY TO SHOW FILAMENT AND EYELET.

Monochromatic Screen for Optical Pyrometer. Temperatures can be measured with an optical pyrometer using the total visible spectrum but if this is done errors are apt to be introduced and observers may differ widely in their readings owing to the color difference between the comparison source and the source studied. This difficulty can be overcome and a much more accurate brightness match made by using a so-called monochromatic screen in the eyepiece of the pyrometer.

¹ Watson and Zabel: *General Electric Review* (Feb., 1932) 120.

Advantages of Red Screens.—For the most part red glass screens have been used for the following reasons: (1) At low temperatures, the red radiation first becomes visible and thus readings may be made at a somewhat lower temperature with the red glass; (2) the color change for a change in wave length is much less in the red part of the spectrum than in the green, which makes the red the better part of the spectrum for this work; (3) better monochromatism can be obtained in glass of this color; (4) by using a red screen when measuring a temperature so high that a rotating sector or absorbing glass is necessary, the transmission

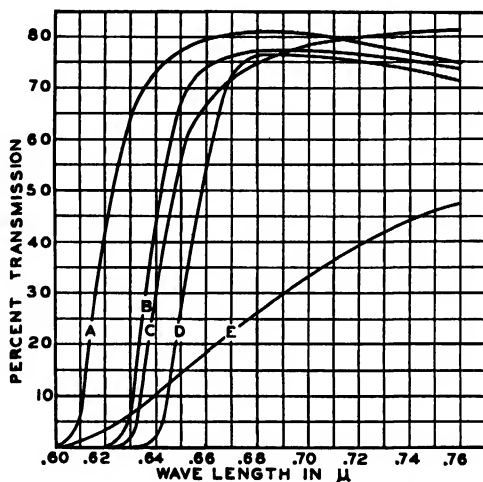


FIG. 5.—SPECTRAL TRANSMISSION OF VARIOUS RED GLASSES

Curve C for Jena red 4512, 2.93 mm. thick.

Curve E for Jena red 2745, 3.2 mm. thick.

Curve A for Corning high-transmission red, marked 150 per cent, 5 mm. thick.

Curve B for Corning high-transmission red, marked 50 per cent, 5 mm. thick.

Curve D for Corning high-transmission red, marked 28 per cent, 6 mm. thick

of the sector or absorbing glass that must be used to reach a particular temperature is greater for the longer wave length than it is for the shorter wave length.

In Fig. 5 are shown the spectral transmissions of several red glasses that are nearly enough monochromatic for use under various conditions. The glass having the spectral transmission shown by curve A does very well for a commercial pyrometer for low temperature ranges because the amount of light transmitted is so great. The glass having the transmission shown by curve E was formerly used for this purpose. As the effective wave length for this glass varies about twice as much as for the other glasses, it is not as satisfactory. The glasses having the transmission shown by curves B, C and D are suitable for the most accurate work.

Effective Wave Length of a Monochromatic Screen.—While it is necessary to use a colored glass in the eyepiece of the pyrometer to overcome certain color differences, an optical pyrometer can be so calibrated and so used as to make unnecessary a knowledge of the extent to which the screen is monochromatic. For some purposes, such as extending the temperature scale, a study of bodies that are not black, etc., it is necessary to know the value of the effective wave length of the screen used.

In using the pyrometer, it is the integral luminosities through the red glass that are compared, for which reason the effective wave length of the red glass screen for a certain temperature interval has been defined as the wave length for the definite temperature interval for a black body, such that the ratio of its radiation intensities equals the ratio of the integral luminosities through the screen used.

Knowing the spectral transmission of the red glass, it is possible to calculate the effective wave length, λ_e , for any temperature interval by means of the following equation:

$$\frac{\int_0^\infty J(\lambda T_1) V_\lambda t_R d\lambda}{\int_0^\infty J(\lambda T_2) V_\lambda t_R d\lambda} = \left(\frac{J(\lambda T_1)}{J(\lambda T_2)} \right)_{\lambda_e} \quad [3]$$

where $J(\lambda T)d\lambda$ is the radiant intensity, as given in Wien's equation, for the wave-length interval from λ to $\lambda + d\lambda$; t_R is the spectral transmission of the red glass; V_λ is the luminosity, and $J(\lambda T)V_\lambda t_R d\lambda$ the luminous intensity from the source at temperature T_1 that is transmitted by the red screen. These integrals can be computed by the step-by-step method with sufficient accuracy for this purpose.

Pyrometer Filaments.—Some care is required in the selection of the pyrometer filament. Carbon filaments are quite satisfactory for low temperatures but they will not have a very long life if operated at a high temperature. Tungsten pyrometer filaments are just as good as carbon filaments and have a long life if not operated at a brightness above that necessary to match a black body at the temperature of melting palladium (1828° K.). They are often constructed with a small bend at the exact point where the filament is to be observed. A small pointer is sometimes used to help locate the exact spot. The 2½-mil (0.063-mm.) filaments require about 0.46 amp. to apparently match in brightness the black body at the temperature of melting palladium. One lamp that has been in use almost every day for about two years when first calibrated required 0.4573 amp. to apparently match the black body at the temperature of melting palladium; after about two years of use, it required 0.4578 amp. This difference in current corresponds to about 1° C.

Measuring the Current through the Pyrometer Filament.—For the highest accuracy an ammeter is not suitable for measuring the current through the pyrometer filament. Some form of potentiometer must be used.

If the same potentiometer is used to measure the current through the lamp being studied and the pyrometer a great deal of time is wasted in changing the potentiometer for each reading. A good method, which is at the same time quite accurate, is to use the deflection potentiometer principle. The regular Leeds & Northrup potentiometer lends itself readily to such adaptation. By connecting a millivoltmeter or a galvanometer of the proper sensitivity in series with the standard resistance and between the binding post marked *Br* and a traveling plug inserted in the proper place on the dial, pyrometer currents can be read very easily to one part in three or four thousand. The readings can thus be made very rapidly and at the end of the set these same readings can be checked on the potentiometer. This makes the current readings practically independent of the constancy of any deflection instrument. With a switch in this millivoltmeter line, the potentiometer is left free to check any other current, such as the one through the lamp that is being investigated.

Calibration of Optical Pyrometers.—Questions are often asked concerning the starting point for the calibration of the pyrometer. To make a completely independent calibration of any pyrometer would be a great undertaking. Fortunately, this is not necessary or desirable. If one has to calibrate an ordinary mercury thermometer at about 100° C., it would be calibrated by immersing the thermometer in steam. If a higher point is wanted some material with a melting or boiling point in the proper region might be used, and the calibration made at the melting or boiling point, as the case might be. The temperature of boiling water is defined as 100° C. but the temperature of the other points in this region are used with just as little question and with just about as much confidence as this one. Probably to a lesser extent the same condition exists at high temperatures. The temperature of either melting gold or palladium is constant and well known. It only remains to bring the standard radiator, that is, the black body, to either one of these definite temperatures and from this to calibrate the pyrometer. In this case, the pyrometer filament is matched in brightness with the image of the black body across which it is seen through the eyepiece of the pyrometer.

Calibrating an Optical Pyrometer from a Source at One Standard Temperature.—The standard radiator at the standard temperature gives one point on the calibration. The entire calibration of the pyrometer can be obtained from the black body at the one temperature if the proper equipment is available. A second point on the calibration may be obtained by taking readings of the current through the pyrometer filament for an apparent brightness match with a rotating sector or absorbing glass of known transmission, between the pyrometer lamp and the standard black body. This will give a measure, in terms of the pyrometer current, of a brightness that is some known fraction of that of the standard radiator at the standard temperature. If monochromatic

radiation is used, it is easy to calculate the temperature T_2 of the black body corresponding to this current through the pyrometer filament—that is, to this measured brightness—from T_1 , the standard temperature, by the following formula derived from Wien's equation:

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{\lambda \cdot \log R}{c_2 \log e} \quad [4]$$

where R is the transmission of the sector, and λ is the wave length used. If the measurements are made with a red glass in the eyepiece, the temperature corresponding to this fraction of the brightness of the standard black body can be calculated just as before, except that the effective wave length of the red glass for the temperature interval is to be used.

Extending Temperature Scale.—The filament of the pyrometer lamp should not be heated to too high a temperature if it is to hold its calibration for any length of time. A safe temperature for a tungsten filament is somewhere in the neighborhood of 2000° K. Since it is often necessary to measure temperatures much higher than this, some means must be provided for this purpose. The observed brightness of the furnace at a high temperature can be reduced by the use of a rotating sector or absorbing glass of known transmission. In this case, the temperature of the furnace is to be calculated from the temperature corresponding to the current through the pyrometer filament and the transmission of the sector or absorbing glass used, by means of equation 4, except that for R use the reciprocal of the transmission of the sector or glass; then T_2 will come out greater than T_1 . A convenient method is to work out such extrapolated temperatures for the various sectors and absorbing glasses that are to be used, and plot the extrapolated temperatures against the temperatures as determined from the pyrometer reading. Such curves can then be used with any pyrometer using the same red glass, providing the same sectors or absorbing glasses are used.

Error of Wien's Equation.—Wien's equation is generally used to calculate temperatures from brightness measurements. This equation does not fit the experimental evidence except for small values of the product λT . Table 1 shows just what errors are obtained in the use of this equation rather than Planck's more exact form. The results for true temperature were obtained by calculating the higher temperature

TABLE 1.—*Corrections to be Added to Temperatures Obtained from Wien's Equation to Reduce Them to What Would Be Obtained from Planck's Equation ($\lambda = 0.665\mu$)*

TEMPERATURE, DEG. K	CORRECTIONS TO TEMPERATURE
2000	— 0 01
2600	— 0 05
3000	— 0 3
3600	— 1 5
5000	—15 6

from 1828° K. and wave length of $\lambda = 0.665\mu$. From Table 1 it can be seen that Wien's equation is quite satisfactory for $\lambda = 0.665$ and for temperatures up to about 3600° K., since the error obtained by its use is less than the experimental error.

Standard Lamp for Calibrating Optical Pyrometers.—It is very troublesome to operate a standard black body every time it is necessary to calibrate an optical pyrometer. Much time can be saved if a tungsten lamp with a filament of a suitable size is standardized so as to have the same brightness, as observed with the optical pyrometer, as the standard black-body furnace for a particular temperature. The lamp may also be standardized for other temperatures and thus, by its use, the pyrometer can be calibrated very easily.

Tungsten filaments have been found to depart markedly from Lambert's cosine law² in their radiation. To avoid error due to this cause care must always be taken to determine the temperature of circular filaments by measuring the brightness of the central part of the filament. For this reason the pyrometer filament should always be parallel to the background filament. This, of course, requires that the pyrometer filament be much smaller than the image of the background filament.

Several such lamps with tungsten filaments about 7 mils in diameter were calibrated at Nela Park about 20 years ago and are still the standard of brightness for wave length 665μ and temperatures 1336° and 1829° K.

The tungsten lamp with wire or a ribbon filament that is used as a secondary standard for calibrating an optical pyrometer may be calibrated; that is, the relation between the current through the filament and its temperature given so that the entire calibration of the pyrometer can be checked by the use of the secondary standard not only for the low points but even for the extended scale if the extended scale does not go beyond the safe temperature of the operation of a tungsten-filament lamp (i.e., about 2500° K. for a gas-filled lamp). Dr. Chaney³ and his co-workers of the National Carbon Co. have shown that the positive crater of the arc between certain well prepared carbons is so constant in its brightness temperature, which they give as 3814° K., that it can be used as a secondary standard for this high-temperature region.

Absorbing Screens for Optical Pyrometry.—A sector that has been very carefully calibrated, if used properly, is without doubt the best means that can be used for cutting down the apparent intensity of a source that is being studied. For commercial work, however, absorbing glasses are generally used, and when properly calibrated and properly used are very satisfactory. When it is necessary to use glass absorbing screens, the main requirement is to have a screen that approximates a neutral

² A. G. Worthing: *Astrophysical Jnl.* (1912) **36**, 345.

³ Chaney, Hannister and Glass: *Trans. Electrochem. Soc.* (1935) **67**, 107.

tint sufficiently well to enable comparisons in brightness to be made by different observers with the same results. The degree to which it is necessary for the absorbing screen to have a spectral transmission independent of the wave length depends on the so-called monochromatic glass used in the eyepiece. It is evident that if this eyepiece glass is absolutely monochromatic, any absorbing glass will answer.

In Fig. 7 are shown the spectral transmissions of a piece of Noviweld (curve C) and a piece of Jena absorbing glasses (curve B). Either of these glasses is nearly enough neutral tint for use with the red glasses having transmission curves shown by B, C and D in Fig. 5.

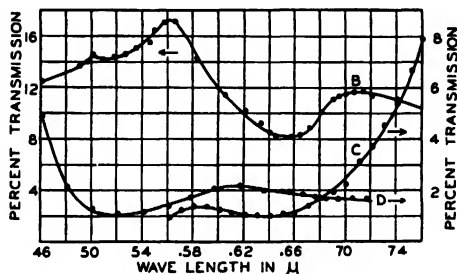


FIG. 6.—SPECTRAL TRANSMISSION OF VARIOUS ABSORBING GLASSES.

Curve B, Jena absorbing glass 1.5 mm. thick

Curve C, Noviweld obtained from Corning Glass Works, shade about 6.

Curve D, Leeds & Northrup absorbing glass made of purple and green glass

Dependence of Temperature on Various Conditions.—The temperature depends on the following conditions:

1. The Constant c_2 . The value of c_2 that seems to fit all the experimental data is $14,320\mu$ degrees.

2. Brightness. A very great advantage of the optical pyrometer in measuring temperature is due to the relation between a change in the brightness and the corresponding change in temperature. At 1000° K. for red radiation ($\lambda = 0.665\mu$), the brightness varies about 22 times as fast as the temperature. At 2000° K. for red radiation the ratio is about 11.

3. Clean Optical Parts. The first thing to keep in mind is that the optical pyrometer is a calibrated instrument and must be handled as such. All the optical parts of the instrument should be kept clean. The actual reduction error due to the transmission on the objective lens if the lens becomes dirty is not very great. The transmission has to be reduced by about 10 per cent to cause an error of 10° at 1500° K. Errors much larger than this, however, are possible if too much dirt is allowed to accumulate on the lens. If the lenses and pyrometer lamp bulb are allowed to become dirty, the dirt interferes with the clearness of the images and thus lessens the accuracy of the setting. They should be

kept clean, but in cleaning them care is required or scratches will be produced, which will interfere with definition.

4. Comparison Source. Great care must be taken not to change the comparison source in any way. In some pyrometers even the position of the comparison lamp must not be changed. In the disappearing-filament type small changes in the position of the part of the filament under observation will cause no appreciable error. The filament must not be overheated, since this may greatly change its characteristics. The pyrometer lamp of tungsten, if not used at a temperature higher than 1828° K., will have a long life. The lamps have been aged for a considerable time at a temperature much higher than this, so a current somewhat above that for which it is calibrated will not change its calibration. A good plan is to allow no current higher than that for which it has been calibrated to pass through the filament.

Accuracy Tests.—A number of experiments were made to test the accuracy that might be expected in the use of the disappearing-filament type of optical pyrometer. In the first experiment, readings were made by a number of observers who had no experience in this kind of work; in the second experiment readings were made by experienced observers. The instrument used was the laboratory form of pyrometer shown. The resistance that controls the current through the pyrometer filament was so chosen that the sliding contact had to be moved some distance in order to change the apparent brightness of the filament by an appreciable amount. The current was measured by means of a potentiometer.

In Table 2 are given the results of the first experiment. Observers 1 and 2 were high school graduates with several months experience as laboratory assistants. Observer 3 was a man with several years experience in shop work. Observer 4 was a man with several years experience in a lamp factory. Observers 5 and 6 were girls from the lamp factory; No. 5 had no experience with this kind of work, while No. 6 had had experience with the photometer.

TABLE 2.—*Results Obtained with a Disappearing-filament Type of Pyrometer by Inexperienced Observers*

Observer	Value Obtained for Temperature as an Average of Six Readings, Deg K		Variation of Single Readings from Mean, Deg K
Standards...	1438	1643	
1. L. C	1439	1643	4
2. H. W	1438	1642	3
3. F. G.... ..	1439	1642	2
4. E. H.	1436	1644	3
5. E. W..... .	1436	1636	5
6. L. R.	1436	1640	2

These results show that but a single observer made an error greater than 3° K. in the temperature as obtained from the average of six readings. In no instance was a value of temperature obtained from a single reading that differed more than 5° from the mean of the set of readings. These results are thought to be very good and to indicate the character of results that could be obtained with this form of pyrometer in industrial work. The pyrometer used probably enabled the observers to make much more accurate observations than is possible with a commercial form of the instrument. Even a commercial instrument, however, could be so constructed that good observations could be obtained. In this work, as in almost all work depending on eye observations, a small amount of training makes a great improvement in the accuracy of the results.

The second experiment was more extended and had as an object to test out the constancy of readings of different observers when using a sectorized disk of low transmission or a dense absorbing glass to cut down the apparent brightness of a source studied. The observers who made these readings obtained very nearly the same readings when using the pyrometer directly; that is, with no sector or absorbing glass.

In this experiment, first with two pieces of Jena red glass No. 4512 (spectral transmission shown by curve *C*, Fig. 5) and second with two pieces of Corning red 50 per cent (spectral transmission shown by curve *B*, Fig. 5) in the eyepiece of the pyrometer, readings were made on the apparent brightness of a particular source as observed through a rotating sector with two 1° openings, the Noviweld absorbing glass having the spectral transmission shown by curve *C*, Fig. 6, and through two pieces of Jena absorbing glass having the spectral transmission shown by Curve *B*, Fig. 6. The source used was a 15-mil tungsten lamp operated at a color temperature of 2610° K. The brightness was measured in terms of the current through the pyrometer filament for an apparent brightness

TABLE 3.—*Results Obtained by Experienced Observers Using Different Red Glasses and Different Absorbing Glasses*

Observer	Red Glass Used	Direct	Current through Pyrometer Filament for Apparent Brightness Match with		
			2° Sector	Noviweld Absorbing Glass	Two Jena Absorbing Glasses
I. A. V	Jena No. 4512	0 4343	0 3358	0 3804	0 3547
K. H. M.	Jena No. 4512	0.4343	0 3361	0 3807	0 3546
W. E. F	Jena No. 4512	0 4343	0 3361	0 3803	0 3546
A. G. W	Jena No. 4512	0 4343	0 3358	0 3805	0 3547
I. A. V	Corning Red		0 3380	0 3784	
K. H. M	Corning Red		0 3380	0 3785	
W. E. F	Corning Red		0 3380	0 3783	
A. G. W	Corning Red		0 3378	0 3784	

match. Four observers made the measurements, three of whom had had considerable experience with this kind of work. Values of the current through the pyrometer filament obtained for a brightness match are given in Table 3. The maximum range in this current corresponds to about 1 per cent in brightness; that is, to less than 5° in temperature at about 2500° K.

TABLE 4.—*Corrections to Temperature Measured with Optical Pyrometer*

Temperature, Deg K	Silver Mirror, 94 Per Cent Reflection, Deg C	Clean Glass, 91 Per Cent Transmission, Deg C	Mica, 75 Per Cent Transmission, Deg C
1200	4	6	20
1500	6	10	31
1800	9	14	44
2100	12	19	60
2400	16	25	79
2700	20	32	100
3000	25	40	125

In Table 4 are given the corrections for different temperatures for a piece of glass of which the transmission for the red radiation (transmitted by the red glass) is 91 per cent, about the average of the different clean lamp bulbs that have been measured. A small amount of blackening on the glass will reduce this transmission to 85 per cent or even lower. For a transmission of 85 per cent the corrections would be about twice those given for a transmission of 91 per cent. There are included in the table corrections for different temperatures due to loss of light from reflection from a clean silver mirror whose reflection for the red radiation is 94 per cent. The corrections, of course, would be very much increased if the mirror became tarnished. The corrections in Table 4 were calculated from the measured transmission of the glass or the reflection factor of the silver mirror by means of equation 4.

Polarization.—To test the effect of polarization with this type of pyrometer, a large nicol was mounted directly in front of the pyrometer lamp and readings were made with the position of the nicol varied with respect to the pyrometer filament. With a red glass before the eyepiece of the pyrometer, the apparent brightness of the background (a black body) was about 1 per cent more when the nicol was so set that the transmitted light was polarized in a plane at right angles to the pyrometer filament than with the nicol turned through 90° . Since the source is known to be free from polarization, this shows that the effect of polarization is almost negligible even when all the light is polarized. From work on diffraction around the pyrometer filament, a small difference would be expected even with this instrument.

Position of Rotating Sector.—If the rotating sector is used to cut down the apparent intensity of the background, care must be taken as to the location of the sector. There is a marked difference in the results of temperature measurements, depending on whether the sector is located near the objective lens or as near as possible to the pyrometer lamp. There is also a difference depending on the relative position of the openings in the sector and the source, providing the source is a lamp filament.

TABLE 5.—*Errors in Temperature Measurements Due to Improper Location of Sector*

	Position of 2° Sector			
	Near Lens		Near Pyrometer Lamp	
	Opening of Sector Parallel to Back-ground Filament	Opening of Sector Perpendicular to Back-ground Filament	Opening of Sector Parallel to Back-ground Filament	Opening of Sector Perpendicular to Back-ground Filament
Current, amperes through pyrometer filament for brightness match	0 3332	0 3354	0 3357	0 3337
Apparent relative brightness	0 9390	0 9950	1 0000	1 0000
Temperature of background for these readings, deg. K	2263	2275	2277	2277

In Table 5 are given results of a test showing the effect of the position of the sector. A 15-mil (0.381-mm.) tungsten lamp operated at a brightness temperature of about 2275° K. was used as a background and readings were made on the current through a 2½-mil tungsten pyrometer filament, for an apparent brightness match with a sector having two 1° openings. From the table it can be seen that the position of a sector of this size can cause an error of about 14° K. for this condition if care is not taken as to its location. When a sector is used, it should be rotated so fast that no flicker is noticeable. Not only is an error apt to be made if the sector is not rotating fast enough, but the flicker is bothersome in making accurate brightness comparisons.

Errors Due to Various Causes.—In Table 6 is given the variation in extrapolated temperature due to a variation in initial temperature, in effective wave length, in transmission of absorbing glass or transmission of sector, and in current through the pyrometer filament. First, is given the change in the temperature due to one percentage variation of each and then some other possible variation. This table shows that in extrapolated temperatures quite an error is allowable in the effective wave length or the transmission of the sector or of the absorbing glass without any great error in the final results. Any error, however, in

calibrating at the initial temperature will cause a much larger error in the final result.

TABLE 6.—*Changes in Temperature of 2400° and 3000° K. Extrapolated from 1800° K. as Initial Temperature, Using Wien's Equation, Due to Various Changes*

Variation Leading to Error	Percentage Change			Actual Change, Deg. K.		
	1800°	2400°	3000°	1800°	2400°	3000°
Change of 1 per cent initial temperature	1 0	1 30	1 70	18 0	32 0	50 0
Change of 3° K. in initial temperature				3 0	5 0	8 0
Using a wave length, 1 per cent in error		0 30	0 70		8 0	20 0
0.001 error in wave length . . .		0 05	0 10		1 2	3 0
If in extrapolating the λ_c of red glass between 1300° and 1800° K. is used (see Fig. 4)		0 10	0 30		2 4	7 5
Calibrating pyrometer filament against tungsten lamp as background that was standardized with a red glass different from one used in pyrometer being calibrated. Suppose λ_c to change from 0.665 μ to 0.650 μ				3 5		
Error of 1 per cent in value used for transmission of sector or absorbing glass		0 26	0 32		6 2	9 6
Variation of 1 per cent in current through 2½-mil pyrometer filament	0 5	0 70	0 80	9 0	16 0	25 0

General Notes.—If an optical pyrometer, as shown in Fig. 2, is constructed so as to transmit sufficient light to enable temperatures to be measured as low as 1000° K., this pyrometer will transmit too much light for comfort at high temperatures. The diaphragm before the eyepiece telescope at *E* can be constructed as shown so as to have several openings of various sizes. For a low temperature, the larger opening is to be used, thus transmitting more light, while for a higher temperature a smaller opening should be used. In this manner the same instrument can be used over a wide range without discomfort.

If too large an opening⁴ is used before the telescope eyepiece, the pyrometer filament will not disappear against the image of the background but there will be dark streaks along the edges of the pyrometer filament. If these dark streaks are too prominent, it is impossible to make consistent settings. The resolving power of whatever eyepiece is used should be so adjusted that the pyrometer filament disappears as a whole; that is, so that neither dark nor bright streaks can be seen along the edge of the

⁴ Worthing and Forsythe: *Phys. Rev.* (1914) 4, 163.

Fairchild and Hoover: *Jnl. Optical Soc. Amer.* (1923) 7, 543.

pyrometer filament. If for any reason it is necessary to use an eyepiece of large resolving power, a good disappearance can be obtained by increasing the size of the cone of rays that reach the pyrometer filament from the objective lens. If this is pushed too far, an objective lens with a very large aperture is required. If the light is too intense for comfort, it can be cut down by using one or more additional red glasses before the eyepiece. If two red glasses are used in the eyepiece, the addition of a third red glass will reduce the apparent intensity of the image by about 50 per cent. If more light is desired for sources at lower temperatures, it is often a help to remove one of the two red glasses that are being used. If two red glasses are being used and one of them is removed, the brightness of the image observed will appear about twice what it did with two red glasses. If no sector or absorbing glass is used with the pyrometer there will be very little effect on temperature measurements if the number of red glasses in the eyepiece is changed. If a sector or absorbing glass is used corrections will have to be made for the change in effective wave length for the number of red glasses used.

Observations on Non-black-body Sources.—Optical pyrometers are generally used to measure the temperature of furnaces where approximately black-body conditions exist. However, it is often convenient to study non-black bodies with an optical pyrometer and to assign a temperature to a brightness of a non-black body as if it were a black body. From the definition of a black body and Kirchhoff's law, all other bodies that owe their brightness to thermal causes alone are less bright when at a particular temperature than a black body at the same temperature. Thus, if the temperature of any hot non-black body is calculated from a measurement of its brightness as though it were a black body, values that are lower than the true temperature will be obtained. The temperature obtained, however, is the temperature that a black body must have in order to have the same brightness for the particular wave-length interval as the body being investigated. It is called black-body brightness temperature or, shortened, "brightness temperature." When a non-black body has a brightness temperature of 1500° K. for $\lambda = 0.665\mu$ it has the same brightness as a black body at 1500° K. for this wave-length interval. The difference between the true temperature and the temperature thus obtained varies from a few degrees, for such a substance as untreated carbon, to more than 200° C. for such a metal as polished platinum at its melting point.

Emissivity of Non-black Bodies.—The ratio of the brightness of a non-black to that of a black body at the same temperature is called its emissivity. For any source with known emissivity, true temperatures can be obtained from brightness temperatures. By emissivity of a particular source is meant the ratio of the brightness, for a particular wave-length interval, of the source to that of a black body for same wave-

length interval and at the same temperature. The emissivity may vary with the wave length as well as with the temperature. Thus, the brightness temperature will in general depend upon the wave length used.

The relation between brightness and true temperatures as derived from Wien's equation is

$$\frac{1}{T} - \frac{1}{S_\lambda} = \frac{\lambda \log e}{c_2 \log e_\lambda} \quad [5]$$

where T is the true temperature, S_λ the brightness temperature and e_λ the emissivity for wave length λ .

As an example of emissivity the following may be mentioned: For platinum the emissivity for the red ($\lambda = 0.665\mu$) varies from 0.36 for a temperature of 1000° K. to 0.32 for a temperature of 1400° K. For tungsten the variation for the red ($\lambda = 0.665\mu$) is from 0.46 for $T = 1200^\circ$ K. to 0.42 for $T = 2800^\circ$ K. For the blue for tungsten ($\lambda = 0.467\mu$) the change is from 0.49 for $T = 1200^\circ$ K. to 0.45 for $T = 2800^\circ$ K. The emissivity of carbon for the red ($\lambda = 0.665\mu$) varies from 0.86 for $T = 1200^\circ$ K. to 0.79 for $T = 2200^\circ$ K. Iron oxide has a very high emissivity, being about 95 per cent for the red radiation for $T = 1400^\circ$ K. The values of brightness temperature obtained by observations on heated iron oxide with an optical pyrometer are very nearly equal to the true temperature.

[For discussion of this paper, see page 202]

Some Metallurgical Applications of the C-SiC Thermocouple

By G. R. FITTERER*

(Chicago Meeting, October, 1935)

By means of the C-SiC thermocouple¹, liquid metal temperatures have been found to vary much more than was previously supposed, and fortunately these variations can be directly associated with some of our former knowledge which combined to form the "art" of liquid-metal manipulation.

COMMERCIAL DEVELOPMENT OF THIS DEVICE

Several types of installations are operating in different plants. There are so many variables in steel plants in regard to operation, procedure, arrangement of pouring platforms, ladles, etc., that most of the installations now in service in this country are "tailor-made"; nevertheless, it is felt that satisfactory gains have been made, inasmuch as each installation has indicated some effect of temperature upon the metallurgical operation, and has pointed the way toward technical and financial benefits.

In most cases, it has been necessary to accumulate the temperature data until sufficient metallurgical information is available for the drawing of conclusions. When mechanical difficulties have been eliminated, a distinct correlation of these factors has been obtained. The installations now in service are used for the determination of temperatures in the basic open-hearth furnace prior to tapping and in ladles from both acid and basic furnaces prior to pouring. Some of the installations are in shops making the higher priced steels; others are in "tonnage shops." The errors of human element, smoke screens and emissivity corrections connected with the use of the optical pyrometer do not affect the C-SiC thermocouple readings. The accuracy of the C-SiC thermocouple and the temperatures measured are discussed later in this paper.

TEMPERATURE VARIATIONS OF LIQUID PIG IRON

One well-known discussion between the blast-furnace and open-hearth (or Bessemer) departments has occurred intermittently for more

Manuscript received at the office of the Institute, Sept. 23, 1935.

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¹G. R. Fitterer: A New Thermocouple for Temperatures Up to 1800° C. *Trans. A.I.M.E.* (1933) **105**, 290.

than 40 years. The open-hearth or Bessemer operator will state that he is getting "off" or cold pig iron, which is causing some difficulties in the manufacture of the steel.

The blast-furnace operator then checks the analysis and optical temperature and shows that they were within the usual limits, and the open-hearth operator returns to his own department for the answer. If the complaint came originally from the rolling mill department he will attempt to trace the difficulty to that department, inasmuch as he can show that, according to the charge, analysis and optical temperature, the heat in question was made in the usual manner. In general, such problems are abandoned without any definite conclusions having been reached. Sometimes they are traced to some operative procedure.

THE MIXER AS A SOURCE OF TROUBLE

Investigations with the C-SiC thermocouple have indicated that there is at least one definite reason for this old question. Between the blast-furnace and open-hearth departments, the liquid pig iron can change in both composition and temperature, because the metal is carried to the mixer in submarine ladles, held in the mixer for hours, and then taken in transfer ladles to the open hearth or Bessemer. Very little investigation of the mixer furnace has been made because formerly it was considered to be simply a retaining vessel, having no effect on the iron because of the large masses involved. That this is not true is shown in Fig. 1, which indicates the temperature variation of a 1000-ton Bessemer mixer. In this particular instance, two Bessemer furnaces were in operation and 25 tons of metal was taken from the mixer every eight or ten minutes. Fig. 1 shows that as long as the mixer furnace contained a large quantity of liquid pig iron, it maintained its temperature within the range 2300° to 2350° F. However, as the amount of metal was depleted in this vessel, the heat content of the metal was not sufficient to maintain this temperature, therefore there was an appreciable and rapid heat loss from that point until a new cast from the blast furnace was brought to the mixer. This metal, which probably was at 2600° F. when it went into the mixer, was mixed with cold metal at 2190°. The temperature after a thorough mixing was about 2360°. That this trend is not accidental is indicated in the second portion of Fig. 1, in which an almost identical trend is indicated for another day in the same mixer. Hence it is apparent that the Bessemer furnace was operating on liquid pig iron that varied nearly 200° F.

The fact that temperature variation plays a large part in the successful operation of a Bessemer furnace is well known, but it seems only logical to conclude that the metal entering the converter should be at a constant temperature. Also, such a decrease in temperature rapidly decreases the

carbon content of the pig iron by precipitation. This factor of composition could be controlled by simply maintaining a constant temperature in the mixer.

Some considerable data are at present being correlated to show the effects of such temperature variations on the resulting Bessemer steels.

Reasons for Temperature Changes in the Mixer.—The cooling effect is probably caused by the draft of cold air passing through the mixer from the pouring to the charging spout while the transfer ladle is being filled. This chills the back wall and when the mixer is again rotated to the horizontal position the cold refractories cool the metal.

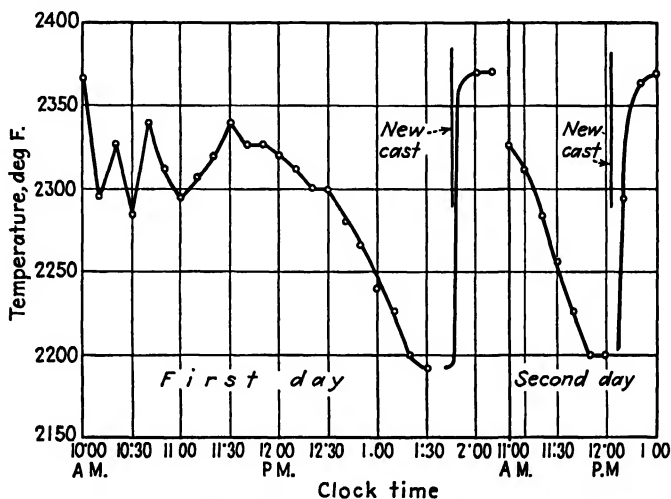


FIG. 1.—TEMPERATURE VARIATION OF A 1000-TON BESSEMER MIXER.

In an open-hearth shop, this effect may be even more marked, particularly in good times, when often several furnaces require hot metal from the mixer at one time. This depletes the metal in the mixer quickly and there may be a long lapse of time pending a new cast. The question arises as to whether the mixer should keep its status of a mere retaining vessel or should have a temperature-control apparatus correlated with burner equipment, which would always keep the temperature constant.

At the two points mentioned where the metal temperature dropped to 2190° F., the metal is near the eutectic temperature for 1.5 per cent Si iron. Hence, one would say that if this mixer had not received new metal when it did, solidification would have taken place, but in this work it was found that a tremendous amount of heat is given off during the solidification of this type of iron. This would tend to allow only extremely slow solidification of so large a mass. Thus this heat of solidification acts as a safety valve and probably prevents considerable trouble in this furnace by holding the metal at the eutectic temperature

until the next cast arrives from the blast furnace. This fact will be illustrated in the mixer ladle application

VARIATIONS IN BLAST-FURNACE TAPPING TEMPERATURES

The above investigation would indicate, of course, that both the blast-furnace and the steel-furnace departments could use the mixer furnace as an excuse, in case of difficulty. It has been found, however, by means of the C-SiC thermocouple, that the variations in tapping temperatures from both the blast and open-hearth furnaces are much greater than has been supposed. Table 1 shows some variations in the tapping temperatures of various blast furnaces working on both basic and Bessemer irons. One temperature obtained in the manufacture of ferromanganese is also given therein. As would be imagined, this temperature is generally far higher than any attained in ordinary pig-iron manufacture. Variations of blast-furnace temperatures, of course, would alter somewhat the curves of Fig. 1. Although most of these temperatures are sufficiently low to use a Pt-PtRh couple encased in sillimanite or fused silica and finally a tube of graphite, previous experience has indicated considerable variation of calibration in the platinum couple due to carbon monoxide poisoning. Further, difficulties with the refractory tube discourage this type of temperature measurement.

TABLE I.—*Variation in Blast-furnace Temperatures*

RUNNER TEMPERATURE, DEG F	TYPE OF IRON
2612	Low Mn basic
2603	Low Mn basic
2465	Low Mn basic
2467	Medium Mn basic
2524	High Mn basic
2500	High Mn basic
2650	High Mn basic
2415	Bessemer
2616	Bessemer
2556	Bessemer
2728	Bessemer
2700	Bessemer
2885	Ferromanganese

VARIATIONS OF HOT-METAL TEMPERATURES IN THE CAR-TYPE LADLE

The Ladle Refractories Are Hot.—Another item, also, should be taken into consideration. The temperature of the metal in the submarine or car-type ladle, in transferring the hot metal from the blast furnace to the mixer, varies under different conditions. If a submarine ladle has just been emptied, it is hot when it is returned to the blast furnace and the type

of cooling curve shown in Fig. 2 is obtained. This is gradual and has certain flat points, which indicate a tendency toward supercooling of the metal followed by a rapid precipitation of graphite or kish. The evolved

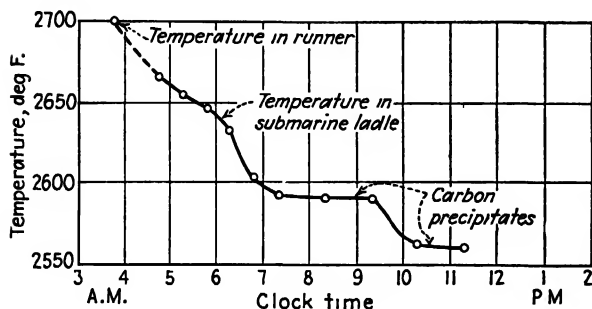


FIG. 2.—COOLING CURVE OF A HOT 100-TON SUBMARINE LADLE.

heat of solution maintains a constant temperature for hours. This is the case referred to in the mixer-furnace studies.

The Ladle Refractories Are Cold.—Another type of cooling curve is shown in Fig. 3. When a cold submarine ladle is taken to the blast

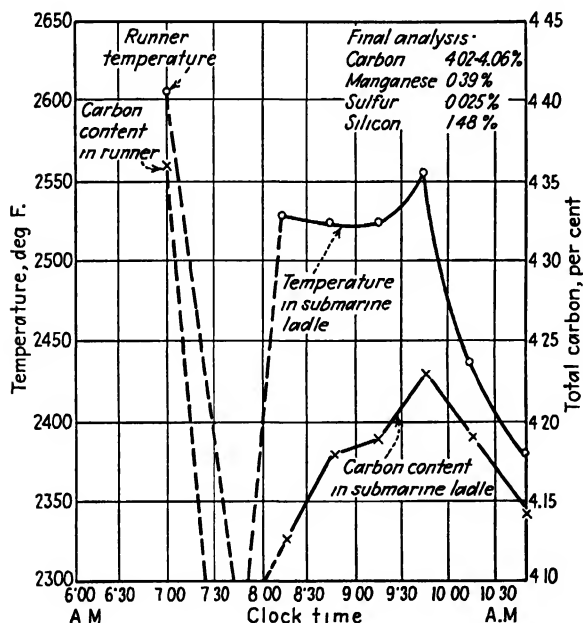


FIG. 3.—TEMPERATURE AND CARBON VARIATION IN COLD 100-TON SUBMARINE LADLE OF DIRECT MOLD IRON.

furnace, there is an instantaneous chilling of the metal in the vicinity of the refractory walls; then, after a few hours, a temperature equilibrium between the center and the outside metal together with the refractories is established. During this period, carbon is absorbed because of the

increased temperature, thus tending to saturate the metal. After equalization in both composition and temperature, a gradual temperature drop occurs together with the normal precipitation of graphite or kish. The rapidity with which the composition follows a change in temperature is remarkable. The condition of the submarine ladle thus determines to a

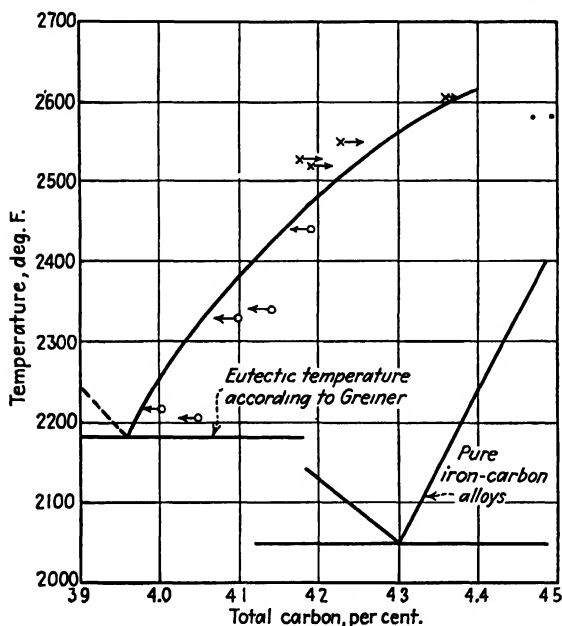


FIG. 4.—SOLUBILITY OF CARBON IN IRON CONTAINING 1.5 PER CENT SILICON AND 0.50 PER CENT MANGANESE, DETERMINED FROM COOLING CURVE OF 100 TONS OF METAL.

large extent at what temperature the iron enters the mixer—also its composition.

Development of a Phase Diagram.—Data can be obtained from the points in Fig. 3 to indicate an Fe-C phase diagram for pig iron containing 1.5 per cent Si and 0.50 per cent Mn. If the carbon content of the pig iron is plotted against the temperature at the time the sample is taken, the carbon saturation can be obtained for this type of pig iron, as shown in Fig. 4. Some of the points plotted were taken during a temperature increase, whereas others were taken during a decrease in temperature. In the former case, the carbon content of the metal was increasing, by virtue of increased temperature and its contact with kish on the surface. In the latter case, it was decreasing, because of the decreasing temperature and decreasing solubility. The arrows in the figure indicate whether the metal was absorbing or precipitating carbon. A saturation line has been drawn between these points, and it is felt that this type of investigation is even better than the attempt to obtain true equilibrium in small melts, inasmuch as both decreasing and increasing points are indicated. Fig. 4, on which the curve for pure iron and the curve just

discussed are indicated, also shows the marked effect of 1.5 per cent Si and 0.5 per cent Mn upon the solubility of carbon in iron. Further work along these lines will be to establish a series of curves for a number of commercial irons. A more accurately analyzed series of points of this type might easily lead to determinations such as heats of solution of carbon, etc. This curve certainly indicates that one should never use the pure iron-carbon diagram in an effort to explain blast-furnace or pig-iron phenomena.

This was the first attempt at determining phase diagrams with the C-SiC thermocouple. Several systems of somewhat more complicated nature are now being studied by means of cooling curves on 1000-lb. lots of steel. Every grade of steel has its own melting and freezing temperature range and there is an almost endless job ahead to satisfy the need in this field.

EFFECT OF CASTING TEMPERATURES UPON LIFE OF INGOT MOLDS

The most important economic discovery by means of the C-SiC thermocouple is that the life of an ingot mold is determined largely by the temperature at which the mold itself was cast.

In the plant where the foregoing tests on temperatures of pig iron were made, ingot molds were made from a grade of Bessemer pig iron. The iron was taken from the blast furnace in mixer or car-type ladles and held in the yards or the foundry until the molders were ready to cast. It has been shown in the foregoing studies that the temperature at which each ladle of metal would arrive at the foundry is dependent upon the temperature of the cast at the blast furnace and the temperature of the ladle refractories at the time of filling, together with the holding time.

Another variation that was encountered in the pouring temperature of molds was found to be similar to the temperature variation of a mixer furnace. When the mixer ladle holding 100 tons was emptied into a series of ordinary stoppered ladles each holding 20 tons, it was found that the temperature of each succeeding small ladle was considerably lower than that of the preceding one. Because of this the five small ladles taking metal from the same mixer ladle were all poured at different temperatures into the molds. Whenever the mixer ladle was tilted, cold air rushed in at the lower manhole and out at the top, thus chilling the refractories in a manner similar to that described for the mixer furnace, and when the small ladle was filled and the mixer ladle returned to the horizontal position, the cold refractories chilled the ladle.

In determining the effect of pouring temperatures upon the life of ingot molds, the temperatures of the small 20-ton ladles just before pouring into the molds were used. These temperatures varied from about 2160° to 2500° F. The only molds that can be used for a study of

this sort are molds that gradually wore out in service; i.e., the walls of the mold gradually became pitted so greatly that the mold had to be discarded. Molds with their sides or bottoms cracked displayed a similar but more erratic trend, due to some severe operating conditions.

When the life of the mold, in terms of the number of ingots poured into it before it was taken out of service, is plotted against its pouring temperature, a curve such as that shown in Fig. 5 is obtained. Pouring near the eutectic temperature, as shown in Fig. 4, results in very high mold life. With slightly increased pouring temperatures, approximately

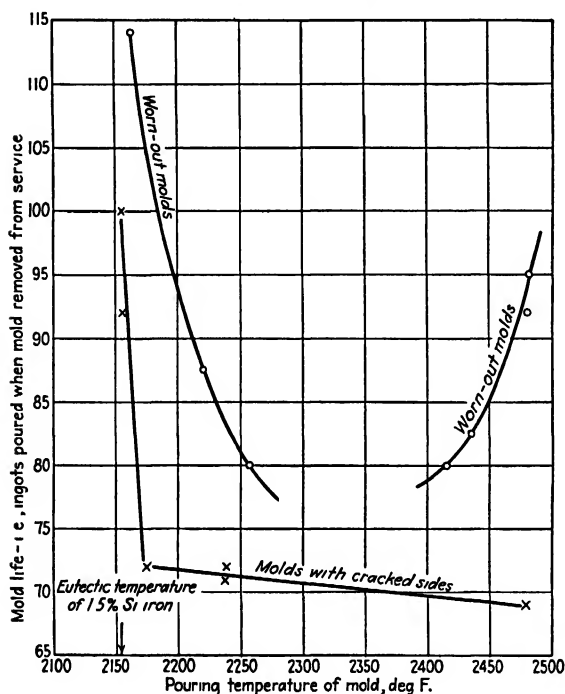


FIG. 5.—RELATION BETWEEN TEMPERATURE AT WHICH MOLD WAS MADE AND ITS LIFE.

100° F. above the eutectic, the life of ingot molds decreases sharply. In the range of temperatures from 2400° to 2500° F., the mold life increases rapidly with increasing pouring temperatures.

Information of this type is very difficult to obtain because sometimes the life of an individual ingot mold must be followed for a period of more than a year. This is the reason there is not a considerably greater amount of such information. These studies are continuing, and some of the results now being obtained follow this trend.

METALLURGICAL EXPLANATION OF MOLD-LIFE PHENOMENA

Best of all, however, these results have a distinct metallurgical explanation. When metal is poured into the mold at eutectic temper-

ature, all of the excess carbon above the eutectic composition has previously been precipitated in the ladle. Also, because the eutectic temperature is the lowest temperature at which this material may remain molten, the metal solidifies instantaneously after it enters the mold. Only one thing will keep the metal molten for a short period of time before solidification, and that is the large heat of fusion of this type of metal, as was mentioned previously. Because of this, the inner surface of the ingot mold is free from segregated areas of graphite and the structure is homogeneous throughout.

However, this is not true of ingot molds poured at 100° F. above this temperature. Ingot molds poured at approximately 2250° to 2400° F. are sufficiently high in temperature to contain from 0.05 to 0.20 per cent carbon in excess of the eutectic at the time the metal enters the mold. Therefore graphite is precipitated in segregated areas, but before it can be eliminated by rising in the liquid metal, the latter solidifies and traps the graphite. Later, when liquid steel is poured into a mold of this type, it attacks these segregated graphitic areas and causes pitting and quick rejection of the mold from service.

In the region of temperatures from 2400° to 2500° F. the life of the molds improved. This may be explained by stating that there is sufficient time between the filling of the mold and the solidification of the metal to allow the excess graphite to float upwards and be eliminated from the mold before solidification takes place. Hence, this higher temperature range of pouring simulates the conditions in structure and life of molds poured at the eutectic temperature. It will be most interesting to see what the life of ingot molds will be when poured above 2500° F. It is possible that they may exceed the values obtained by eutectic pouring. Further proof of these results is indicated in Fig. 3, which shows definitely that graphite precipitation quickly follows a drop in temperature. This is also the probable explanation of the effect of superheating of cast iron in the electric furnace.

TEMPERATURE MEASUREMENT OF LIQUID STEEL IN A BASIC OPEN-HEARTH FURNACE

An 11-ft. thermocouple has been installed in a basic open-hearth in such a way that it may be lowered through the roof and immersed 10 in. into the metal through 2 or 3 in. of slag. The furnace has a sloping backwall and the point at which the couple enters the bath is midway between the ends and one-third the width from the front bank. This position represents the deepest part of the bath. Temperatures obtained in this application are representative of only one point in the furnace, but because this point is located at one-half the depth of the bath in its deepest portion, the temperatures obtained are probably representative, or at least relative from heat to heat.

Some values are given in Fig. 6, in which the temperature is plotted against the carbon content for each heat. These are all for steels containing under 0.45 per cent of carbon. The temperatures were obtained during the last hour that the heat was in the furnace and prior to tapping. The temperatures range from 2750° to about 3000° F. All heats that were cold enough to solidify slightly in the ladle are marked with numbers that indicate the weight of the ladle skull in pounds. With one exception, all of the lower temperature heats showed skulls in the ladles. Hence again these thermocouple readings may be correlated with definite metallurgical data. One heat containing 0.18 per cent of carbon had a furnace temperature of 2880° F., and still showed a skull of 9000 lb. This heat may have been held in the ladle for a longer period of time than

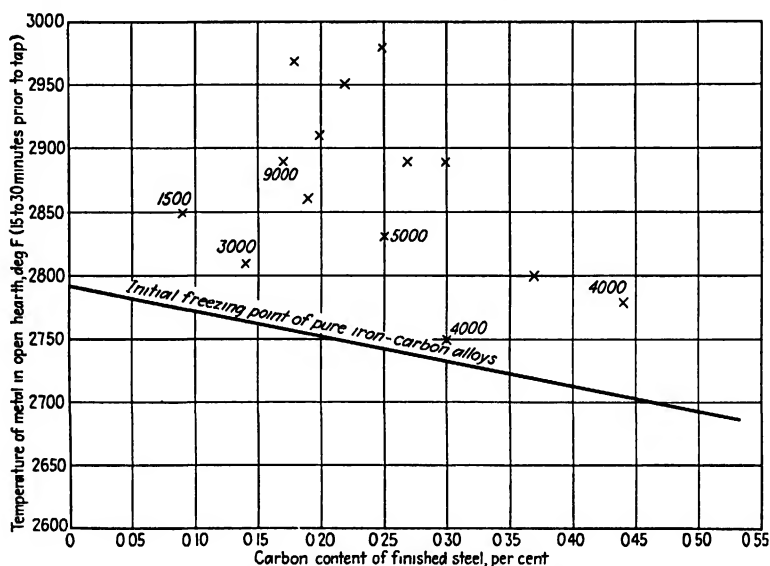


FIG. 6.—TEMPERATURE OF LIQUID STEEL IN BASIC OPEN-HEARTH FURNACE ONE HOUR BEFORE TAPPING. NUMBERS INDICATE LADLE SKULL WEIGHTS, IN POUNDS.

the others that showed skulls. It is quite possible that a more detailed study involving the length of time each of these heats was in the ladle and the temperature of the ladle refractories prior to filling would explain the minor variations shown in the figure for the skulled heats.

It is, of course, not fair to compare the temperatures without considering the composition of the metal, because, as shown in this figure, and as is well known, the higher the carbon content of the steel, the lower is its freezing point. The heats indicating ladle skull in this figure strike a band of points parallel to the iron-carbon liquidus.

It is the belief of the author that if the temperature of the ladle refractories and the time between tapping and pouring were set by prac-

tice according to data of this nature, many of the erratic results in open-hearth and other furnaces would be eliminated. A 1000-lb. skull is desired in some shops and there is no reason why this should not be controlled at will by means of the C-SiC thermocouple.

When the heats without skulls are considered, one wonders at the enormous waste of fuel in overheating such large masses of metal. It would also be interesting to know the effect of these upper and lower temperature heats in producing surface defects, etc. Data of this sort are being obtained at present.

The application of the C-SiC thermocouple to the measurement of steel temperatures in the basic open-hearth is probably the most difficult that will ever be encountered. Problems met in the first installation in the open-hearth furnace have been solved to a considerable extent. Some changes in mechanical operation and design are now being made.

LADLE POURING TEMPERATURES OF ACID OPEN-HEARTH IRONS AND STEELS

The fact that there is a considerable difference in pouring temperatures in acid irons and steels being cast as rolls is indicated in Fig. 7.

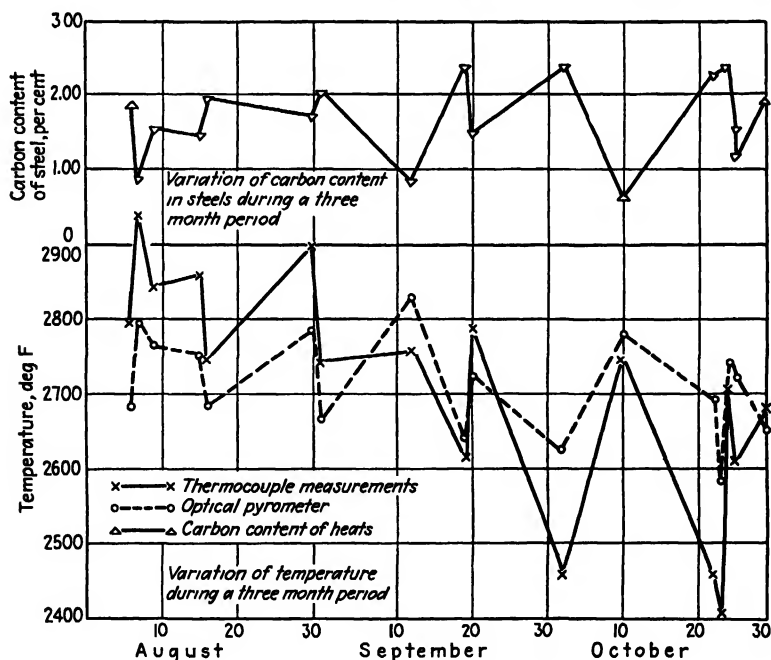


FIG. 7.—ACID OPEN-HEARTH LADLE TEMPERATURES, SHOWING VARIATION OVER THREE-MONTH PERIOD.

Both optical and C-SiC thermocouple readings are shown. The optical readings were taken by sighting on the furnace spout, whereas the

thermocouple readings were taken in the metal in the ladle just before pouring. In some tests only a few minutes elapsed between the determination of the two instruments; in others as much as 24 minutes separated the readings.

The trend through the three months, according to the couple, indicates that in general the efficiency of the open-hearth was decreasing and also that the operation was becoming erratic. Only a few weeks later the furnace was shut down and rebuilt.

It is particularly interesting to note the graph at the top of Fig. 7, in which the corresponding carbon contents were plotted against the date of the heat. When the carbon was high the temperature was low, and vice versa. Hence, with a high carbon the metal appears fluid at a lower temperature by virtue of its lower melting point. The operator then taps his heat correspondingly.

A most interesting metallurgical comparison is obtained by combining the data in Fig. 7 in the manner shown in Figs. 8 and 9, wherein the thermocouple and optical temperatures are plotted against the carbon content. It can be seen at a glance that there is not much variation in the range of temperatures according to the optical. The series of points fall in a region that is somewhat parallel to the theoretical liquidus in the pure iron-carbon alloys and vary only from 2580° to 2840° F. The thermocouple readings, however, vary from 2400° to 2930° F. The figures beside the points indicate the time interval (in minutes) between the optical and thermocouple readings. It must be recalled that each optical reading was made on the metal in the furnace spout, whereas the couple reading was made in the filled ladle.

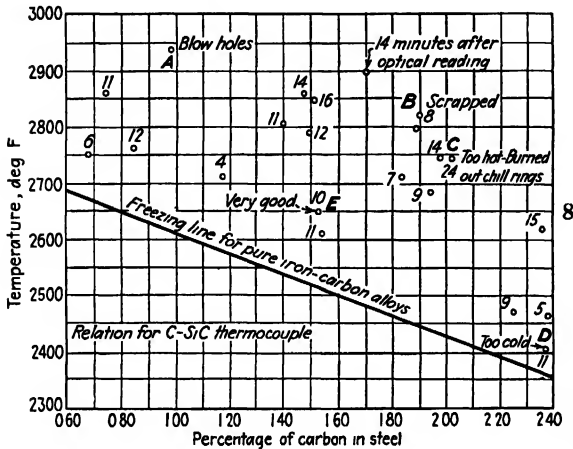
SIGNIFICANCE OF THERMOCOUPLE READINGS IN STEEL LADLES

Pouring Temperatures Too High.—These figures become more interesting when some of the points are studied individually. Heats A and B, as indicated in Fig. 8, were very hot, particularly when compared to the distance from the liquidus. Points A and B were 300° and 375° F. respectively above their corresponding liquidi. Both of these heats were scrapped because of blowholes in the neck of the rolls. They were also both rather high in silicon content, which some operators believe induces nitrogen solubility or compound formation when accompanied by elevated temperatures. Evolution of the gas upon solidification leaves nitrogen-filled blowholes.

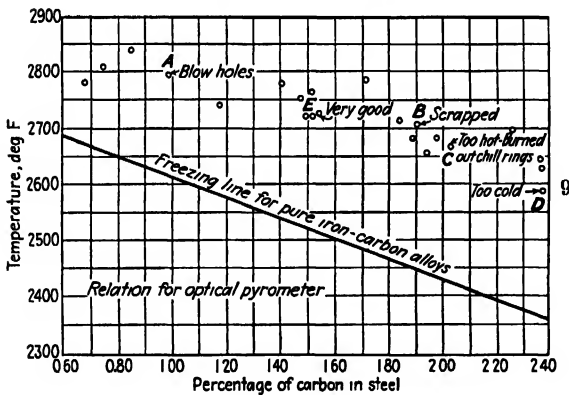
Point C, Fig. 8, indicates a heat that was so hot that it fused with the chill-rings in the sand mold and necessarily was discarded for that reason. It is well to point out that this thermocouple temperature was taken 24 minutes after the optical temperature and yet it was 315° above the liquidus for that metal according to the pure iron-carbon diagram. Also, it was about 80° F. above the earlier optical reading. The temperature

at the time the optical reading was taken was probably closer to 2900° F. when the 24-min. period in the ladle is considered. Cooling curves on such ladles have shown about 10° F. drop a minute.

Pouring Temperatures Too Low.—Point D shows a heat that was discarded because it was too cold and did not properly fill the molds. This was strikingly indicated by the C-SiC thermocouple.



FIGS. 8 AND 9.—COMPARISON OF THERMOCOUPLE WITH OPTICAL PYROMETER TEMPERATURES, ACID OPEN-HEARTH PRACTICE



Proper Pouring Temperatures.—One heat (point E), recorded as excellent, is shown by the C-SiC thermocouple to be about 160° F. above its liquidus.

SIGNIFICANCE OF OPTICAL READINGS

Turning now to Fig. 9 and studying these same heats, A to E inclusive, it is impossible to correlate the optical readings with metallurgical data. The optical temperatures of the scrapped heats show no metallurgical significance in comparison with the good heats. The heats that were found to be too hot, by the C-SiC thermocouple and subsequent

metallurgical data, were tapped at the usual temperatures according to the optical.

STABILITY, CALIBRATION AND REPRODUCIBILITY

A considerable amount of research work has been done concerning the stability, calibration and reproducibility of the elements of this couple. The author's former paper on this subject may be referred to in connection with this type of data.

DISCUSSION

(Alexander L. Feild presiding)

[This discussion applies also to the paper by W. E. Forsythe, which begins on page 171.]

T. L. JOSEPH, * Minneapolis, Minn.—In the past three weeks I have been attempting to get some measurements of temperatures of pig iron in the runner. The investigation is being conducted by the Bureau of Mines in cooperation with the Inland Steel Co. Mr. Scott and Mr. Douglas have been working with me. The first thing we set out to do was to get a temperature measurement in two ways to see how we would check. Altogether we have probably taken 800 or 900 simultaneous readings with a platinum couple placed in a primary porcelain tube, with a secondary carbon tube as protection. Adjacent to this platinum couple, we have a graphite tube about 3 in. in diameter, with a hole about 1 in. in diameter. We sight on the bottom of the graphite tube with an optical pyrometer and take simultaneous readings with the noble-metal couple and the optical pyrometer. Our readings check very well. The average difference between the platinum couple and the black-body optical readings was about 15° or 20°. We feel that there are one or two very critical factors in taking the temperature of iron in the runner. Graphite is a good conductor of heat, and the depth of immersion of the graphite in the metal is therefore critical. With a shallow depth of immersion, sufficient heat is conducted away from the tip of the couple, or the surface on which you are sighting with an optical, to affect the temperature. In other words, there is a temperature gradient in the piece of graphite. If the two tubes are immersed 8 or 10 in., which is feasible, when the iron flows in a good stream or when a dam is built in front of the tubes, we get pretty fair temperatures. We have advanced to the point where we get continuous records of the temperature with a recorder.

We attempted to get some idea as to the error caused by conduction away from the tip, by putting a couple in a bare quartz tube adjacent to these other tubes. We got a higher reading on the bare couple.

We attempted to separate the tip of our tubes from the main body of the graphite with some refractory material, some poor conductor, but have not been able to make such joints gastight. By getting away from surface conditions, which I believe lead to the largest errors with the optical, and approaching black-body conditions by submerging the tube into the bath and by keeping away from smoke between the end of the tube and the observer, fairly good readings can be taken with an optical pyrometer.

I think temperatures taken with the Fitterer couple might be lower than true temperatures because of conduction along the graphite in that couple.

R. H. SWEETSER,† New York, N. Y.—This discussion reminds me of what the American Rolling Mill Co. did in 1923 at its Columbus blast furnaces, and also at the

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† Consulting Engineer, Blast-furnace Practice.

Ashland blast furnace. We had the two types of pyrometers, an optical pyrometer and a stem pyrometer, which had a rhodium-platinum couple encased in fused quartz and then protected with the graphite tube, as Mr. Joseph has described. We took the temperatures of the iron as it came out of the iron notch and over the dam, the temperature of the slag that came out of the iron notch, which we call the "slug," and the temperature of the slag at the flushes. Observations were made every 30 sec., and we had the check-up between the optical and the stem pyrometers. The minute there was any slag showing on the molten iron or any fume, the optical pyrometer could not be used.

The Columbus test was made in May. Later in the summer we made some improvements in the method of reading the stem pyrometers and made tests at the Ashland blast furnace, for temperatures of the molten iron, and checked up with the results obtained in the open hearth and in the steel mill, in the steel made from that pig iron.

We found that "good iron" (iron that was acceptable in the open hearth) had a temperature of 2700° to 2750° F. and the "bad iron" had a temperature around 2400° to 2450° F. The blast furnace was then operated so as not to make any more of that kind of iron (i.e., with temperature around 2400° to 2450° F.). We went far enough to find that iron made with a certain slag temperature had good physical temperature, and the blast-furnace man made that kind of iron thereafter. The iron that went from Columbus to the Middletown plant, of course, went as cold pig, and we could not follow it through very well there. I believe it would be helpful if we could dig up those old records. I will go over my notes when I go home, and I will ask permission of The American Rolling Mill Co. to publish some of those records, because it seems as though we were a little bit ahead of our time.

W. H. SPENCER,* Muskegon, Mich (written discussion).—The temperature of molten cast iron may be obtained with sufficient accuracy for practical purposes by means of the optical pyrometer. The use of the more accurate noble-metal thermocouple is expensive and not very satisfactory under shop conditions. There are certain precautions necessary in the use of the optical pyrometer. Keeping the instrument clean and in good mechanical order, not attempting to read temperatures through smoke or dust, and similar cautions are usually unnecessary. A short discussion of the principle on which the instrument operates may help in obtaining better optical readings.

The optical pyrometer in its usual form consists of a light source that may be varied in intensity or have a variable screen before it. The intensity of the light from the molten metal is compared with the light from the source in the instrument. Under black-body conditions, which may be approached inside furnaces, there would be no need for correcting the observed temperatures for general purposes. When readings are made on molten metal in streams or ladles, a black-body condition does not exist and the observed readings must be corrected. The amount of the correction depends on what proportion of the total radiation is emitted by the body. Materials do not all have the same emissivity rates and therefore require different corrections for their observed optical temperatures. For example, cast iron and slag or iron oxide at the same temperature do not give off the same intensity of radiation. If optical readings are made on the film and on the iron, much higher correction values must be added to the observed temperature on the iron than would be necessary for those on the film in order to obtain true temperatures.

In order to ascertain the proper correction factors to be added to optical readings on molten cast iron and to find why two or more apparent temperatures were possible

* Metallurgist, Sealed Power Corporation.

on the same surface at one time, the following experiments were made. A 3-ton ladle was filled with molten cast iron and then slowly emptied. Two observers with optical pyrometers calibrated by the National Bureau of Standards made simultaneous readings on the surface of the metal in the ladle or in the stream. Each observer read the highest and lowest apparent temperatures each time. A noble-metal thermocouple was immersed in the ladle and true temperatures were read simultaneously with the apparent optical readings. The results obtained by the two observers were averaged for each point. The high and low readings, however, were kept separate

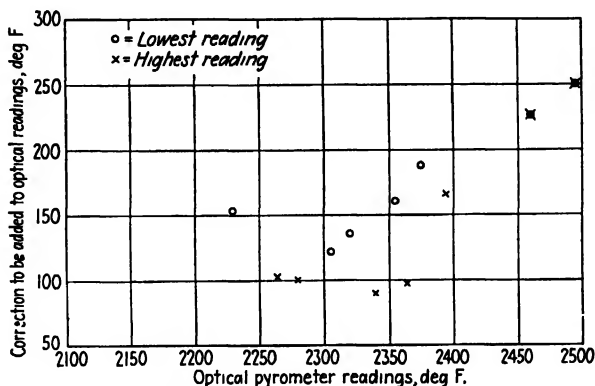


FIG. 10.—LADLE READINGS.

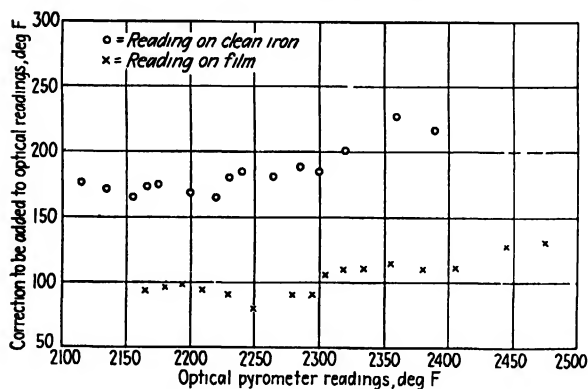


FIG. 11.—STREAM READINGS.

and called film and iron readings. Fig. 10 gives the corrections necessary to be added to the optical black-body readings in order to obtain the true thermocouple temperatures for observations made on surface of iron in ladles, Fig. 11 gives the same information for stream readings.

As shown in Fig. 10, there are two possible readings on the surface of the metal in the ladle at any time. These readings differ from each other about 80° F. If either the highest or lowest possible reading is taken, the proper correction will give a true temperature. Much difficulty in obtaining good optical temperature measurements is due to applying the wrong correction or to obtaining a compromise reading instead of the highest or lowest one possible.

In Fig. 11, for stream readings above the freezing point of iron oxide the highest and lowest possible observations coincide. Below this temperature the readings

lie between clean iron and film readings, as might be expected on a swiftly moving clean iron surface mottled with film.

This information was obtained for a cast iron of approximately the following composition: Si, 1.50 per cent; S, 0.080; Mn, 0.45; P, 0.65, total C., 3.50. It is possible that metal of different composition might change the corrections necessary for film readings.

A. B. KINZEL,* New York, N. Y.—Practically, each of the speakers in the discussion has emphasized the need for getting some object to the temperature to be measured, in a condition equivalent to that of a black body and then proceeding to measure that temperature. This is probably always practical, with the exception of ladle streams from the bull nozzle and runners from the furnace itself. Assume for a minute that we can put a graphite or silicon carbide tube into the bath so as to get the temperature we want fixed at a given point, the problem is then to measure it. We must admit that thermocouples to date have not been very satisfactory.

With platinum type there is a top limit of 1600° C. Even below that temperature gases affect calibration. The Fitterer couple also seems to have limitations. We have had the same problem in connection with welding puddles, and have arrived at a satisfactory solution by a combination of a clear quartz tube and photoelectric cell. Such a tube conducts light through its length without emanating the light from the sides. The light enters at one end and goes right through, as water goes through a piece of copper tubing, which may be twisted in a spiral. We have used such a quartz tube to conduct the light from the source to a photoelectric cell sensitive to red wave lengths. With the photoelectric cell properly calibrated, the human factor is eliminated. This instrument is not in the final stages of development for open-hearth work at the moment, but is called to the attention of this group with the thought that here is a method of attack that seems relatively free from some of the limitations encountered in other types of measurement.

R. L. GOETZENBERGER,† Minneapolis, Minn. (written discussion).—Realizing the demand for a dependable pyrometer that actually does measure speedily the temperature of materials in motion about a steel mill, other metallurgical works, glass plants, and the like, as well as the increasing need for a reliable method of determining accurately the higher temperatures of material while in furnaces without recourse to troublesome base-metal or expensive and likewise bothersome noble-metal thermocouples, the Minneapolis-Honeywell Regulator Co., with its affiliate, the Brown Instrument Co., and in collaboration with steel-mill engineers, has developed the Optimatic, an automatic optical pyrometer that does the work of the disappearing-filament pyrometer, independently of human-eye judgment, automatically, precisely and substantially instantaneously. In producing this manufacturing tool the practical requirements of industry with regard to ruggedness, accuracy and constancy of calibration have been placed foremost.

The rapidity in the functioning of this automatic optical pyrometer is apparent from the fact that it indicates or records to full scale the temperature of a hot body in less than $\frac{1}{2}$ sec. Critical damping is inherent and the chart record shows no overshooting. Hence the device is particularly adapted for use in measuring, without retarding rolling operations or production in any way, the temperature of bars, billets, slabs, sheets, strips, rails, rods, tubes and the like while being processed.

Some of the benefits gained through its application to hot-strip rolling mills are:

1. Enables the holding of the various slab reheating furnaces at the same temperature because it is so sensitive that it detects during the initial stages of rolling

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† Manager, Industrial Regulator Division, Minneapolis-Honeywell Regulator Co.

the slightest unevenness in heating as well as skid marks. Therefore, it becomes the guide for uniform distribution of heat from skid to skid or side to side of furnaces.

2. Prevents controversies between heaters and rolling-mill operators because its record is definite proof of improper processing.

3. The best temperature for removal of scale, cleaning and finishing of the sheet can be ascertained with it.

4. From an analysis of its clear records the best rolling temperatures for different gages, sizes, etc., enabling exact correspondence on subsequent runs, can be determined.

5. Prevents accumulation of rejects by revealing faulty processing in the early stages, hence contributes in no small degree to the reduction of manufacturing costs.

6. Makes possible a permanent temperature record of mill output. This is particularly valuable in the case of alloy steels and for all special orders.

Particularly emphasis has been placed upon the advantages of the automatic optical pyrometer for measuring, with greatest speed, the temperature of moving objects. Also, this instrument possesses unique merit in that it can determine the temperatures of the work within furnaces where the use of base-metal and noble-metal thermocouples, which are often subject to attack by furnace gases, should be avoided. Another application of this pyrometer is the measurement of temperatures in bright-annealing furnaces where the hydrogen, penetrating the protection tubes on base-metal thermocouples, causes the couples to change calibration. Temperatures of molten metals, open-hearth roofs, checker brick, forge furnace walls, etc., are other examples of its adaptability. Whether the heated object be moving or stationary, records and indications are accurate; automatic control is more easily gained and can be accomplished within narrower limits. Furthermore, the automatic optical offers no installation or maintenance problem when applied to new or old machinery. The Optimatic consists of three parts:

1. A water-cooled telescope, or sighting element, that scans the hot body, the temperature of which it is desired to measure. This is spring mounted to a supporting ring in order to eliminate all vibrational disturbances, an essential detail especially when viewing small objects

2. A power supply and amplifier unit, which can be energized from a 25 or 60-cycle alternating current supply, is connected to the sighting element by means of a weather-proof cable.

3. A recorder or indicator, or both, as desired, having standard range of 1200° to 2500° F. or special ones, is wired to the amplifier unit. The speed of chart movement of the recorder is readily varied and automatically may be shifted instantly from slow to fast or vice versa by the passing of the heated target.

The two photocells, the responsiveness of which varies about as the tenth power of the target temperature changes, are mounted in the sighting element. One of these is exposed to light emitted by the target surface, the temperature of which is to be measured. The other, through a simple amplifying circuit, is illuminated automatically by a balancing lamp to maintain a relative value of conductivity as the first photocell changes. Hence the current in this lamp circuit becomes the measurement of temperature.

The photocells are connected as a Wheatstone bridge. An amplifying tube, which becomes the substitute for the ordinary galvanometer of that circuit, magnifies any effect of inequality in the illumination of the two photocells. The fundamental nature of the photoelectric cell, whereby its resistance varies with the amount of light that falls upon it, causes the voltage across the photocell to change instantaneously with the slightest variation in illumination. These hot-body conditions cause the viewing photocell to change its resistance, which creates immediately a voltage modification with the consequence that the grid bias of the amplifying tube is altered. The resultant action from the entire amplifying circuit influences the illumination of the

standard lamp which, in turn, balances out the differences arising from the variations in light emitted by the viewed heated object. It is this balancing principle, which does not prevail with photocell pyrometers incorporating a single photoelectric tube and amplifying stages, that gives the Optimatic circuit stability, nullifies small variations in tube characteristics that might occur during normal service and permits wide voltage fluctuations of factory power supply without creating erroneous temperature indications.

R. B. SOSMAN,* Kearny, N. J.—We were interested in the C-SiC couple as soon as it was announced. The fundamental thing to find out first, obviously, is whether it can be reproduced. We tried making our own couples from graphite tubes and Globar heating elements, which are rods of pure silicon carbide. Three couples were compared at known temperatures between 250° and 1150°C., to see whether we could obtain reproducible readings.

We obtained three fairly straight lines of electromotive force against temperature, the lines crossing the axis of zero millivolts at 8° to 12°C. and crossing 350 mv. at 1055° to 1100°C., when the reference junction was at 15° to 20°. The slopes of the three lines were 321, 327 and 337 microvolts per degree, respectively. This high thermoelectric power, contrasting with 40 microvolts for the chromel-alumel couple and only 12 microvolts for the platinum-10 per cent rhodium couple at 1200°C., is worth emphasizing again as a point in favor of the Fitterer couple. Our experiments thus showed that the couple is reasonably reproducible from a piece of graphite and a piece of Globar. We learned later that it is desirable to heat-treat the couple at a high temperature in the high-frequency induction furnace. The curves can thus be brought nearer together than those of the hit-or-miss couples we prepared. So from the point of view of reproducibility, I think it is a sufficiently reliable pyrometer, provided it represents the temperature of what it is immersed in. That is the critical point.

To obtain information on the question whether an immersed protected thermocouple will give the temperature of liquid steel, we have made a number of measurements of bath temperature in the open-hearth furnace. The experiments were made with a platinum-10 per cent rhodium thermocouple contained in a small protection tube of refractory porcelain, $\frac{1}{4}$ to $\frac{1}{8}$ in. inside diameter with walls $\frac{1}{4}$ in. thick or less. This tube is enclosed in an external protection tube 18 to 24 in. long, with walls $\frac{1}{4}$ to $\frac{3}{4}$ in. thick, made of fireclay, graphite or silicon carbide. At the open end of the protection tube is a water-cooled head, inside of which is the reference junction of the thermocouple. The instrument is inserted through the door, with the water pipes as a handle, and the observer is protected by a sheet of metal. When this pyrometer tube is held for 3 to 6 min. horizontally in the gases and exposed to the radiation of the furnace, the temperature of the thermocouple is in good accord with optical temperature measurements of the inside of the furnace. The couple takes up the temperature of the combustion gases, or the prevailing black-body temperature in the inside of the furnace. But when the tube is put down into the steel, immediately the temperature of the couple falls 30° to 95°C. below the temperature of the steel, as indicated by optical readings on bubbles, tapping temperatures and the like. The lowered temperature was found to hold fairly steady for several minutes. These temperatures are all to some extent approximations, so that the differences stated are not to be taken as accurate, but it was the universal observation that the bath temperatures obtained with thick tubes were low. What is the reason?

One possible explanation is that reactions are going on at the surface of the tube. If you tried to measure the temperature of boiling water by means of a thermocouple

* Research Laboratory, U. S. Steel Corporation.

in a protecting tube made of ice, you would not get 100° no matter how deep the tube was immersed. So if a reaction is taking place on the surface of the pyrometer tube an incorrect though apparently steady reading will be obtained. Even if there is no heat-absorbing reaction, there is bound to be a gradient of temperature in the tube. It has nearly the temperature of the cooling water at the top, and the temperature of the furnace at the bottom. The flow of heat is across and along the tube. Where there is a flow of heat there is a gradient of temperature. So there will always be a set of isotherms within the combination of tubes, and always a difference of temperature between the outside and the inside.

It might be supposed that the experiment just referred to, of putting the tube in the gases and getting a fairly good reading of furnace temperature, would prove that the isotherms are normally far apart in the lower end of the tube. But that state of affairs depends upon free transmission of heat into the surface of the tube by radiation and convection. Put the tube down into the steel and what happens? Almost any object introduced into a steel bath immediately serves as a nucleus for the release of gases. The large and irregular surface of the pyrometer tube may be partly or completely covered with a film of gas, which is an excellent insulator. The isotherms immediately spread down from the cold end and the couple reads low. I put that forward only as a hypothesis, since I have no proof that it is the principal reason why the immersed couple reads low, but the couple unquestionably does read low. From this experience we may infer that whether the thermocouple is a platinum couple or a silicon carbide couple (Fitterer's), the size and composition of the protecting tube have an effect on the observed temperature, lowering it by an amount that at present is unpredictable.

C. H. HERTY, JR.,* Bethlehem, Pa.—When we were working on this problem at the Bureau of Mines in 1929, we tried immersion couples in the induction furnace and the open hearth, and we ran against the proposition of boiling on any tube we put in. If we took the temperature immediately after killing a bath, either in the induction furnace or in the open hearth, the temperature jumped as much as 30° or 40°. If you tried that with the couple temperatures before and after the killing of the heat, did you get any sudden rise in temperature?

R. B. SOSMAN.—These temperatures have been taken in the open-hearth bath where in every instance there has been evolution of gas.

C. H. HERTY, JR.—After you kill the heat and put the couple in, you will not get the gas off?

R. B. SOSMAN.—We have not tried that.

C. H. HERTY, JR.—I always suspected that the boiling from an active heat would drop the temperature on the couple.

R. B. SOSMAN.—We are working on other methods of getting bath temperatures but I am not free to describe them. I think the point can be proved.

J. T. MACKENZIE,† Birmingham, Ala.—On the question of immersion, all we have done has been on cast iron, so I never heard of this gas evolution before. It is very interesting. When the National Bureau of Standards made the original comparative tests for the American Foundrymen's Committee on Gray Iron, it developed a similar setup to the one described by Dr. Sosman, with platinum-rhodium and a very thin porcelain sheath about $\frac{3}{8}$ in. in diameter with a graphite tube around it.

* Research Engineer, Bethlehem Steel Co.

† Metallurgist and Chief Chemist, American Cast Iron Pipe Co.

We made a number of tests on depth of immersion. There is a sharp curve, beginning about zero and rising rapidly to about 6 in., so we have pursued the general policy of using an 8-in. immersion with a 1-in. O.D. graphite tube. There seemed to be no rise in temperature beyond 8 in. I cannot conceive of a 4-in. immersion on the Fitterer thermocouple giving true temperature.

C. H. HERTY, JR.—With a heat on which the slag is much hotter or much colder than the metal, it seems to me that the effect of the slag on the top layer of metal would be so great that with 4-in. immersion it would throw the reading off on the metal being poured, particularly in the first part of the heat.

A. L. FEILD, New York, N. Y.—Graphite is soluble in steel, and in addition to the oxidation reaction Dr. Herty speaks of there is probably solution too. Anyone who has stuck a piece of graphite into molten steel knows that it dissolves fairly rapidly. That also would affect the temperature.

There is another point that seems to me important. Dr. Sosman spoke of the isotherms in graphite. It seems to me there would be at the interface between the graphite and steel a decided drop in temperature, even in the absence of chemical reaction, due to the thermal resistance of the interfacial layer.

R. B. SOSMAN.—We are all familiar with the way graphite oxidizes. It does not melt away smoothly, as a metal melts away. The surface gets into a porous state, for some reason. Some of the particles of graphite oxidize sooner than others, so the net result of the oxidation of graphite in the open is always a soft, porous material on the surface, which ought to be a much better insulator than the original dense graphite. That possibly accounts for the drop in effectiveness after the first reading.

C. H. HERTY, JR.—A good many of the points we are bringing out about this couple, such as the boiling, the gas evolution, the thermal loss, etc., would apply, to some extent at any rate, to anything immersed in an open-hearth bath that has not been killed. I think we ought to take it as a general criticism of the immersion instrument in an open-hearth bath rather than as a criticism of this particular couple, because we have tried a number of different things in an open-hearth bath when boiling and we had the same trouble with all of them.

K. C. McCUTCHEON,* Ashland, Ky.—Dr. Fitterer, in his paper, said that optical temperature readings in connection with bath temperatures or in connection with ladle temperatures cannot be correlated. I think that is not a fact. I believe it is possible to correlate optical temperature readings in a practical way and, when all is said and done, that is what we want to do. We want to make practical use of such temperatures.

It is possible to take temperature readings with an optical pyrometer on the stream flowing into the ladle and arrive near enough to the temperature of the steel in the ladle to hold it the desired length of time to pour it with skull or without skull. Based on the temperature reading it is possible to hold a stated number of minutes and arrive at the desired results.

In addition to that, I think optical temperature readings in the bath can be used under certain conditions. We did a little experimenting with proper temperature for burning in the banks, and found that the reading, if taken on the bank shortly before tap, with the gas off, and if the furnace had been carried at a rather uniform temperature for a considerable time, could be checked by optical reading taken on the stream as it went out into the ladle from the furnace. It is possible, under certain conditions, to correlate readings taken in the bath with pouring temperatures, and it

* Assistant General Superintendent, American Rolling Mill Co.

certainly is possible to make use of optical readings on the stream as issuing into the ladle. We need improvements, I will admit, but practical use can be made even in the present state of the art.

F. M. WASHBURN,* Chicago, Ill.—I should like to bear out Mr. McCutcheon's statement with regard to the use of the optical pyrometer. It has been our experience also that the optical reading on the stream going into the ladle is a valuable one to the open-hearth man. We find that by the use of experienced observers and care in the taking of the reading on the windward side, and other precautions, this optical temperature reading can be used as a basis for the time of holding the ladle to insure the desired pouring temperature.

I am not attempting to minimize the need for the immersion thermocouple, but I would very much question whether the 4-in. immersion of the Fitterer thermocouple in the top of the ladle of killed steel is representative of the temperature throughout ladle. I should be inclined to think that the temperature reading on the stream, even taken with an optical, might be a more valuable criterion.

After all, the open-hearth man is not interested in true temperatures. We do not really care whether we are showing the true temperature or not, so long as it is a temperature to which we can come the next time. In other words, we just have a guide for the operation. Therefore, as I see it, the emissivity of the molten metal, and so on, is really of secondary importance as long as we can give the open-hearth man a temperature to guide him.

A. L. FEILD.—I might add that we suspect the emissivity of steels may vary from one composition to the other.

J. T. MACKENZIE.—I doubt very much whether that is true. The change of emissivity on the iron alloy seems to be the point of solubility, which is also the freezing point, of iron oxide. We made some tests with 14 per cent nickel, 2 per cent chrome and 6 per cent copper, and we do not find any difference in the corrections applied to that.

As far as the absolute temperature is concerned, it is of interest especially from the standpoint of pouring temperatures. In dealing with 2.5 per cent carbon iron, we want to know absolute temperatures, because the freezing point of that iron is very much higher than, say, a pig iron of eutectic composition. It does not seem to make any difference as to the composition of the iron. The point where the optical is indefinite is right at 1375° C. Where I read 1350° I do not know whether the temperature is 1400° or 1450°, but I know that if I read 1500° the temperature is 1650°. From about 1300° on down, again we know what the correction is.

J. J. CURRAN,† Greensburg, Pa.—I am interested in the determination of temperatures in the copper-nickel alloys. The temperature range is very much the same as for steel. Authorities say that these alloys should be poured at 2750°, 2800°, 2850°, and so forth, but they do not determine the temperatures themselves and are rather at a loss to tell anyone else how to do it. I would ask if someone can give me the emissivity factor for Monel metal and alloys of lower nickel content, and the same alloys with a small percentage of silicon. Is there any difference when silicon iron and manganese are present? The National Bureau of Standards, as far as I know, has no factor of emissivity for those alloys.

A. L. FEILD.—I am afraid we do not know any more than you do about the emissivity factor of molten Monel metals.

* Wisconsin Steel Works.

† The Walworth Company.

G. SOLER,* Canton, Ohio.—We have recently placed a Fitterer thermocouple in use to measure ladle temperatures after tapping of 100-ton basic open-hearth heats. To date we have taken 21 temperature readings. We have had various difficulties in the use of this thermocouple, such as mechanical difficulties inherent in the design, proper electrical insulation, and a satisfactory refractory coating for the thermocouple tip. We believe that additional development work will be necessary if a satisfactory thermocouple for practical use in measuring temperatures of basic open-hearth steel is to be obtained.

Temperatures taken in the ladle should provide valuable data for correlation of steel quality with tapping temperatures. However, the open-hearth operator is more interested in controlling temperatures in the bath throughout the refining of the heat in order to obtain closer control of rate of reaction, and state of oxidation of the metal at tap.

We are able to obtain a life of only five heats on the carbon tip we are now using. We feel that better refractories must be obtained for the tip if the thermocouple is to be used in basic steel practice.

F. H. ALLISON, JR,† Vandergrift, Pa. (written discussion).—One of the possible objections to the Fitterer thermocouple in present installations is that it is inserted in the top of the liquid steel in the ladle to a depth of only about 4 in. I wonder whether that is a sufficient depth to give a representative reading for the entire ladle of steel. There is probably some difference in the steel temperature from the bottom to the top of the ladle. Has anyone had any experience along this line which would allow him to state whether the 4-in. immersion gives a reading that is representative of the over-all temperature of the ladle contents?

A. L. FIELD.—Is there anything about the Fitterer thermocouple to prevent making it long enough to get an immersion of 8 in.?

R. B. SOSMAN —There is a serious limitation on the Globars. As they are made longer they become rapidly more difficult to make, and the manufacturer hesitates to guarantee the silicon carbide rods more than 36 in. The price increases much more rapidly than the length.

F. B. FOLEY,‡ Philadelphia, Pa.—In connection with the general discussion of methods of measuring the temperature of molten steel, some schemes tried 20 years ago may be of interest. One method, devised by Mr. Wright, of the Leeds & Northrup Co., made use of a mold, similar to a carbon test mold but having a bulb in the bottom into which a thermocouple was inserted upward through the base of the mold. Readings were taken with a potentiometer while the metal was poured into this small mold, and the maximum temperature was noted and correlated with temperatures obtained directly by means of a platinum thermocouple and with an optical pyrometer. The idea was to calibrate such a device in terms of true temperature. Naturally, the thermocouple in the base of the mold did not attain the temperature of the molten metal.

Another method involved the use of an iron tube, protected by firebrick sleeves and closed at the bottom end with a graphite ladle plug. The construction was similar to that of the plug rods used in ladles. This device was pushed under the slag into the metal and an optical pyrometer was used to sight on the plug at the closed end, which was allowed to come to the temperature of the metal bath. Fumes

* Timken Steel & Tube Co.

† Research Metallurgist, United Engineering and Foundry Co.

‡ Superintendent of Research, The Midvale Co.

formed in the pipe so that it was impossible to get readings that meant anything. It did not seem possible to get rid of the smoke either by thoroughly drying the assembly or by using air to blow out the fumes. Mr. Joseph has suggested that the presence of silica in the graphite might account for the smoke, so that were pure graphite used a clear tube would result.

A. L. FEILD.—There is one remark that probably should be made here in order to make the record more complete, and to be a little fairer to the steel melter who judges temperature apparently with his eye. It is something I have said before. A melter is not called on to go suddenly into some dark room and look at some molten steel and estimate its temperature. If he were, he would probably make all sorts of mistakes. On the contrary, he has the entire history of the heat in his mind when he estimates the temperature. He knows how the furnace has been working, and he knows what type of charge he started with. He knows the rate at which he has been running the furnace, the amount of fuel, and so forth. In other words, while he judges the temperature with his eye, he introduces a number of other factors as mental corrections. For all we know, he may often go more largely on what he knows about the heat than by what he can judge by his eye. Furthermore, the pouring test from a small spoon is a great deal more than a simple estimate of the temperature with the eye. I say this because Dr. Forsythe, who is the last authority on the subject of the accuracy of the eye, at least in a purely quantitative way, says the eye is not valuable in estimating temperature. It probably is not. It would be interesting to have some molten steel in a dark room at a known temperature and ask the melter to guess its temperature, or whether it was hotter or cooler than his usual pouring temperature.

E. E. THUM,* Cleveland, Ohio.—I want to ask Dr. Forsythe to clear up a point that has been raised, at least inferentially, once or twice during the morning as to what is practical temperature and what is absolute temperature. He might be able to tell us whether there is any physical meaning of the term 2000° C. (as an example), or whether it is merely an idea gained by extrapolation of the formulas he has given us.

A. L. FEILD.—I have been in steel plants in fairly recent years that did not have an optical pyrometer. If they had one, it had been hidden away in storage.

G. B. WATERHOUSE,† Cambridge, Mass.—That does not mean they did not have temperature-measuring devices of some kind.

A. L. FEILD.—Of course, thermocouples for heat-treating, and so forth.

G. B. WATERHOUSE.—I do not mean that, either. The open-hearth pouring test and all such things are temperature-measurement devices. Look at the roof in the open hearth. Is the refractory dripping? There are various kinds of indications like that.

W. E. FORSYTHE.—I should not like to pass on the question as to whether an optical pyrometer or some thermocouple pyrometer should be used for measuring high temperatures. As has been said, no thermocouple is known that is at all reliable at very high temperatures. However, for moderately high temperatures, that is, around 1500° C. (2750° F.) and under most industrial conditions, both are subject to serious errors, which means that precautions must be taken in their use. Thus far no one has produced a material that will stand up very long at such temperatures, particularly if immersed in such a substance as liquid steel. There is also the question whether the

* Editor, *Metal Progress*.

† Professor of Metallurgy, Massachusetts Institute of Technology.

thermocouple is at the temperature of the bath in which it is immersed. Conduction of heat and reactions between the protection tube and the bath are apt to introduce serious errors. With an optical pyrometer or radiation pyrometer, the surface conditions of the body of which the temperature is to be measured, as, for instance, liquid steel, introduce serious errors. Smoke and dust in the line of sight also introduce errors. It just happens that the problem I have been working on, that is, studying the temperatures of incandescent lamp filaments, seems to make it necessary to use the optical pyrometer.

A high temperature such as, say, 2000°C . (3632°F .), is not merely an extrapolation of some formula but is as definite as any of our theoretical considerations. Lord Kelvin defined temperature in terms of the efficiency of an engine working in the well-known Carnot cycle. The efficiency of such an engine depends upon the temperature of the source and upon the difference in temperature between this source and the lower temperature used. Thus, if this temperature interval is doubled, for the same temperature of source, the efficiency of the engine will be doubled. This defines the temperature interval.

It can be shown that this thermodynamic temperature is the temperature that one would get if he could use a gas thermometer and use as the working substance a perfect gas; that is, one that exactly obeys for all temperatures the law that the product of the pressure and volume equals a constant times the temperature. In the use of such a thermometer, the change in pressure for a change in temperature is generally measured because it is easier to measure than the change in volume. If any real gas is used as the thermometric substance, corrections must be worked out, since real gases do not obey the gas law. Dr. Roebuck, of the University of Wisconsin, and some others who have studied problems of gas behavior can tell us how to work out these corrections. The change in temperature is proportional to this change in pressure, using a perfect gas or corrected to a perfect gas, of course. However, it is practically impossible to find a substance that can be used as the container of the gas; certainly it will not last very long at high temperatures if inserted in such a material as molten steel. Dr. Sosman some years ago used a gas thermometer up to about 1550°C (2822°F .), which is about the upper limit at present.

Another way of obtaining thermodynamic temperatures is the use of a black body and the equations that tell us how a black body radiates its energy. These equations were derived using a thermodynamic temperature and hence can be used to calculate temperatures from measurements of the intensity of radiation from a properly constructed black body.

M. J. BRADLEY,* Philadelphia, Pa.—Perhaps no one outside of the Leeds & Northrup Co. appreciates as well as we do the limitations and shortcomings of the present optical pyrometer. This instrument has been a subject for concentrated research study for the last couple of years. It is in a large measure criticisms from the users in the steel plants that contribute to improvements to better meet the users' requirements. We have to know what is demanded in order to produce an ideal instrument to meet all conditions. Leeds & Northrup have tested a great number of lamps used in optical pyrometers and are not satisfied that they are readily interchangeable with individual calibration. As Mr. Forsythe said, we have developed a flat-sided lamp of which the sides are related to each other at a definite angle that eliminates parallax images. (We are supplementing the optical with a radiation type of temperature-measuring equipment, which also has a definite field of application.)

* Leeds & Northrup Co.

W. J. REAGAN,* Oakmont, Pa. (written discussion).—Most of our experience has been in determining the temperature of 0.60 to 0.90 carbon steel, all fully killed. The majority of the work has been done with the disappearing-filament type of optical pyrometer. We have recently placed in service a similar type of instrument in which a test mark disappears in an illuminated field. We have been able to obtain quite consistent results with either instrument but cannot check one against the other. The results we obtain are apparently of value only to ourselves. They are not comparable with results obtained in other plants on similar grades of steel and using the same type of instrument. We have had considerable difficulty maintaining the calibration of the disappearing-filament instrument. Our experience with the other type has not been sufficient to warrant any comments on its value. We attempt to check the accuracy of our instruments by checking them against a standardized thermocouple installed in a small electric furnace and by sighting upon disks of various materials suspended in the furnace. The temperature of this furnace is limited to 1200° C. (2192° F.) This kind of check is not wholly satisfactory, apparently because of too low a temperature for checking purposes. This check is only for the low end of the scale, while the instrument is used on temperatures in the neighborhood of 1600° C. (2912° F.).

Supposing that our instruments are correctly calibrated, we find that their use in the plant should be standardized, to obtain relatively accurate results. Temperature determinations of molten steel should be taken as nearly as possible at the same point and at the same time in each heat. Readings should be taken at the same point in the stream of metal. In determining tapping temperatures we endeavor to sight on the stream of metal at a point about halfway between the spout end and the ladle, a distance of about 4 ft. Temperatures at this point are found to be higher than those taken at the spout end, because of the breaking up of the smooth stream of metal into a more straggly one. The cause for the higher readings at this point is not clear, being ascribed to interreflection caused by the breaking up of the smooth stream of metal and also to progressive oxidation. While temperatures taken at this point are higher than those taken at the spout end, they seem to be more accurate as to true temperature values than those showing the lower values. Because smoke, gases, etc., obscure the vision of the observer at this point, temperatures of metal while it is being tapped into the ladle are not reliable.

Temperature readings of steel in the furnace (where the results are of value) can be determined by inserting a cold rod into the metal; the resulting boil will be of sufficient intensity to cause enough metal to appear to allow a reading to be taken with the optical pyrometer. A skilled observer may obtain fairly accurate results at this point, and I believe such readings to be of greater value than readings taken when the metal is running into the ladle.

Determining metal temperatures in the furnace by obtaining slag temperatures with the optical pyrometer are wholly unreliable. On groups of heats a close check may often be made between slag temperatures, metal temperatures by means of the rod boil, and temperatures taken at tapping. Other groups of heats show absolutely no relation whatsoever. The point in the manufacture of steel at which the liquid molten steel is most clearly visible for temperature measurements with the optical pyrometer is during the pouring of the steel from ladle to ingot mold. In our practice, with all bottom-cast ingots we have visible a stream of metal about 2½ in. in diameter and from 4 to 5 in. long. As a rule this stream is smooth, therefore the readings obtained give a lower value than similar readings taken on a more straggly stream. While our tapping temperatures give more accurate readings by sighting on a straggly stream of metal, our pouring temperatures taken on the smooth stream give relatively lower values, but much better values for relative comparisons from heat to heat, owing to the absence of smoke and gases.

* Edgewater Steel Co.

There are several other methods of determining steel temperatures. Perhaps the most valuable one is by the use of the residual manganese content of the metal before deoxidation. At this point in the heat conditions are as near equilibrium as it is possible to have them in an open-hearth furnace. For a given manganese content in the charge and a constant iron oxide content in the slag, the manganese increases as the temperature increases, or for a given manganese in the charge and a constant temperature the manganese increases as the iron oxide in the slag decreases. With a constant pig and scrap charge very close temperature estimates may be made. Other methods of temperature determination are: rate of carbon drop, amount of skull in the ladle and of course the regular spoon test for fluidity.

In practice we usually use a combination of these methods, but in spite of their value we must still rely upon the eye and experience of the melter to obtain temperatures that are neither too hot nor too cold.

G. R. FITTERER (written discussion).—Several of the discussers considered a depth of immersion of 4 in. inadequate. I have always recommended a depth of immersion of at least 6 to 8 in. but I wish to submit the following data, which show conclusively that even a 3-in. immersion is satisfactory.

Cooling curves through the freezing point (eutectic point) of 100 lb. of pig iron were obtained on couples of two lengths with two depths of immersion each. The pig iron was saturated at all times with carbon by means of a 1-in. layer of petroleum coke.

TABLE 2.—*Effect of Depth of Immersion on Measured Freezing Point of Cast Iron*

Experiment	Total Length of Couple, Ft.	Length of Couple from Hot to Cold Junction, In.	Depth of Immersion, In.	Distance from Metal Surface to Cold Junction, In.	Cold-junction Temperature, Deg. F.	Initial Temperature, Deg. F.	Freezing Point (Eutectic Pig Iron) Corrected for Cold-junction Variation, Deg. F.
1	7	31	3	28	68	2408	2023
2	7	31	10	21	71	2128	2006
3	7	20	3	17	68	2188	2013
4	7	20	10	10	71	2088	2012

The maximum variation shown (Table 2) is 17° F., and within these limits there seems to be no variation with the depth of immersion or the distance of the cold junction from the metal surface; in fact, the readings are lower for deeper than for more shallow immersions. These variations, although very small, are contrary to the expectations of the discussers. Also, the initial temperature of immersion, or the start of the cooling curve, had no effect. At the freezing point in each of the above experiments the temperature was maintained at a constant value for more than 15 min., thus giving a very definite point.

Let us not forget that in practice we always have a slag blanket which heats the couple some 3 to 12 in. (in ladles) above the metal surface. In the experiments just mentioned there was no slag, only about one inch of petroleum coke, above the metal. Dr. Sosman stated that the immersion is limited to small depths. I have inserted this couple to 2 ft. in some cases.

Several of the discussers are apparently under the impression that this couple was immersed bare so that the graphite tubing was in direct contact with the liquid slag

and metal. This is not so. A coating material has been developed, which will admirably withstand the action of both metal and slag. One of the newly designed ladle couples has just finished a replaceable tip life of more than 50 immersions. The life is somewhat less than this in basic electric-furnace practice and, at present, is about one-fifth with the basic open-hearth practice. However, some proposed changes in the composition of this coating material will unquestionably greatly increase this life. The cost of maintenance in 40-ton acid open-hearth ladles has been reduced to less than one cent per ton. The relative cost in larger basic ladles is proportionately lower because of the tonnage but higher because of the reduced life.

I cannot check the phenomenon mentioned by Dr. Sosman concerning the lowering of temperature due to boiling action. It has been my experience that when the couple has been preheated to very high temperatures in the open-hearth gases, the couple will, when immersed in the steel, indicate a lower temperature. However, if the couple is pulled out of the furnace and allowed to cool slightly below the metal temperature and then reimmersed it will increase to the previously indicated metal temperature.

A very slight boil has been noticed even when the coated couple is immersed in the open-hearth metal but this is not by any means comparable to the boil that occurs when a bare graphite tube is inserted. When the couple is inserted cold it will produce a boil, as will, also, a rod. This would check Dr. Herty's observation. However, when the couple reaches temperature equilibrium as indicated by the potentiometer the boiling practically ceases. I prefer to preheat in the gases to above the probable temperatures before immersion. When this is done only a very slight boil is observed. I have felt that this slight boiling is desirable because it serves as a gentle stirring action, thus adding convection of heat to its conduction and giving a more average temperature of the bath.

Dr. Kinzel says that the temperature limitation of the Pt-PtRh couple is about 1600° C. and that apparently my thermocouple also has its limitations. I would be the first to admit that all thermocouples have their limitations but I also am glad to say that my thermocouple will withstand service as high as 2000° C. (3632° F.). Repeated heating to this temperature will not alter the calibration or decompose either of the elements.

The impression seems to have been obtained that I stated that the optical pyrometer was useless. I stated that I have not been able to correlate optical temperatures with metallurgical data but that I have done this successfully with the C-SiC thermocouple. I believe the optical pyrometer has some limited applications and that only a very few of these are in metallurgical operations. The reason that I have devoted the last several years to this thermocouple development was that vast experience with the optical pyrometer only served to indicate its limitations to me.

An emissivity correction factor is necessary for every grade of steel and every type of slag. Today practically all of our corrections are based upon the slag and "pure" iron data described by the foremost high-temperature pioneer, George K. Burgess, in 1919. These are still being used for the myriad of ferrous metals, with few exceptions. The problem of determination of emissivity correction for all analyses of slags and metals and their variation with temperature has always seemed to me to be an endless and experimentally impossible job. The variation of this emissivity factor with temperature is not even considered in many steel plants. It is used as a constant at all temperatures.

All of the discussion in this paper was concerned with the original installations of my thermocouple. Since Jan. 1, 1936, the development of this device has been returned to me. At the date of this publication all but one of the old installations have been replaced with newly designed couples, all of which are working in a highly satisfactory manner with regular production.

Origin and Growth of Graphite Nuclei in Solid and Liquid Iron Solutions

By H. A. SCHWARTZ,* MEMBER A. I. M. E. AND WOLFRAM RUFF†

(Chicago Meeting, October, 1935)

THE spheroidal form of the temper carbon nodules in malleable cast iron and of the graphite mottles of "mottled" cast iron suggests that in both all the graphite in a given mottle or nodule grew from a single center of crystallization or nucleus.‡ There is, however, a distinct metallographic difference between the mottle and the nodule; the area of mother metal impoverished in combined carbon by the crystallization of graphite in a mottle is practically coextensive with the ramifications of the graphite, while the impoverished zone of metal corresponding to a given nodule is always larger, and usually much larger, than the approximately spherical mass of graphite crystals forming the nodules. Furthermore, the mottle probably is formed during freezing and the nodule almost always at a considerably lower temperature.

Assuming that the nodules or mottles can be used as a measure of the existing nuclei (capable of germination) we propose to record certain observations as to the graphitizing reaction in the light of the number and habits of growth of these nuclei.

The present authors, in cooperation with others¹⁻⁷, have reported upon various cognate aspects of the problem. The fact that temper carbon is a mass of flakes and not a solid granule has become well recognized since the introduction of an improved polishing technique^{8,9,10} for cast iron. The problem of deriving from the circular planar intercepts of a mass of spheres of varying sizes their number and size distribution in space has also been satisfactorily solved^{12,13}.

GROWTH OF NUCLEI IN WHITE CAST IRON

It has already been shown^{1,3} that the progress of graphitization with time is usually consistent with the assumption that nodules grow in size

Manuscript received at the office of the Institute March 5, 1935.

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‡ Gray iron may be regarded as a metal in which mottles are so numerous and/or so large that all adjacent mottles have coalesced. The number of existing nuclei then is no longer capable of direct determination.

¹ References are at the end of the paper.

rather than in number but that exceptions to this rule exist. As an exemplification of the growth of temper carbon nodules certain specimens used in an earlier investigation¹⁴ were measured as to the number and diameter per unit area of the intercepts of these nodules by the metallographic plane.* The metal contained, as cast, 2.30 per cent carbon, 1.20 silicon, 0.29 manganese, 0.156 phosphorus and 0.048 sulfur.

The observed area for each specimen was about 1.67 mm. wide and about 14 mm. long, representing the entire cross section of the specimen except a decarburized layer at each surface. Counts and measurements were made at 150 diameters on material of three different heat-treatments, the data being shown in Table 1. The number of nodules less than 0.1,

TABLE 1.—*Size Distribution of Spherical Nodules Growing at 900° C.*

Time	1 Hr.	8 Hr.	24 Hr.
NODULES PER CUBIC MILLIMETER			
Maximum diameter of nodules, mm	0.120	0.147	0.167
Diameter, max.	6.87	7.48	19.79
0.9 max.	9.42	16.87	18.38
0.8 max.	14.90	30.11	45.47
0.7 max.	28.81	65.47	61.42
0.6 max.	44.07	130.16	81.40
0.5 max.	62.68	102.06	40.10
0.4 max.	63.89	109.06	22.68
0.3 max.	123.63	125.07	54.45
0.2 max.	109.78	100.14	94.45
0.1 max.	2,482.	6,252	11,892
Total excluding smallest	464	687	438
Total	2,946	6,939	12,330
Percentage of graphite	0.30	1.50	1.25

the diameter of the largest nodule, is uncertain. It depends primarily upon counting all the graphite points of less than the minimum diameter (about one millimeter on the print) and no others. All fields contain an immense number of such spots often poorly visible. A little exploration at 1000 dia. suggests that any points visible at 150 dia. (50 dia. at the negative enlarged three times) are graphite. Some nodules, however, might be overlooked. Too much reliance must not be placed upon this series of numbers, however. Fortunately, it will appear later that they represent little graphite. The count was made in selected portions of the

* It is advisable to use the earlier and cruder polishing methods, which, owing to tearing out of some metal, show more clearly the areas occupied by nodules than would the finer detail of the more carefully polished specimen.

entire field, using only about one-eighth of the total area and portions where visibility was at its best.

A statistical consideration of the variation, in individual fields for each specimen, in number of the nodules larger than 0.1 the maximum diameter, indicates that the probability that these figures would vary to the observed extent by random chance is perhaps one in two hundred. The observed differences are thus believed to be real, though they are not proved to be so.

It is not certain whether the increase in number of the very small particles with time is real or due only to increasing visibility with time. Their existence in specimens quenched from 900° C. casts a doubt upon earlier attempts²¹ to explain them as representing the stable eutectoid. *Excluding the fine particles* we may take as a first approximation the assumption that the number of nodules and hence of nuclei is nearly

TABLE 2.—*Comparison of Aggregate Volume of Nodules with Volume of Graphite Therein*

Temperature, Deg. C	Time, Hr.	Graphite, Per Cent		Volume of Nodules per Cu. Mm., Cu. Mm.	Percentage of Graphite by Volume in Nodules
		By Weight	By Volume		
900	1	0 30	0.90	0 054	16 6
900	8	1 50	4.50	0 193	23.3
900	24	1.25	3.75	0 280	13.3
740	96	1 43	4.29	0.082	52.3

independent of time at a given temperature. It may be that this approximate constancy is due to the combined effect of the birth of new nodules as time goes on (or their increased visibility) and their coalescence under surface-tension forces.

A similar investigation of a specimen of the same metal heated 96 hr. at 740° C. and containing 1.43 per cent graphite showed 82 nodules per cubic millimeter, excluding the smallest size, and 9013 including that size. Comparison of these numbers with those of Table 1 leaves no doubt that the nodule number is not solely a function of the material but also of the temperature at which the nodules grew. If nuclei, then, are preexisting entities, we must assume that the ability of a given nucleus to grow is a function of temperature.

It is well known that the form of the carbon varies with the temperature at which it crystallized^{15,16}. Such expressions as "crablike" and "sprawly" are found in the literature describing the character of temper carbon nodules grown at high temperature.

We are now in a position to express quantitatively the geometric distribution of carbon in temper carbon nodules by comparing the

aggregate volume of spherical nodules with the volume of graphite computed from the analytically determined amount. For this purpose it suffices to consider that the metal is three times as dense as graphite (approximately $\frac{7.5}{2.5}$). Table 2 shows such a comparison from the data of Table 1 and those for the material graphitized at 740° C. The proportion of the sum of all the spherical volumes circumscribing temper carbon that is actually occupied by carbon evidently grows smaller as the temperature increases. The differences in the last column between the three figures of 900° C. are probably not significant. Apparently the graphite is packed about three times as compactly in nodules growing at 740° C. as in those growing at 900° C.

A qualitative explanation for the greater compactness of nodules crystallizing at low temperatures is that a thin platelike crystal cannot penetrate the nearly solid metal during growth, and therefore crumples up. A more formal quantitative explanation may be found in the following.

Consider a stream of carbon atoms, migrating along parallel paths, from a region of high concentration near cementite inclusions to one of lower concentration near graphite. Consider a particle of graphite of needle form lying with its axis parallel to the direction of flow. Will such a particle grow primarily in length or in thickness?

The rate of approach of graphite is a function of temperature and the carbon gradient of the solution. The rate at which carbon can be deposited on existing graphite—that is, the crystallization velocity—is a function of temperature. If the crystallization velocity is high compared with the migratory rate, the small area at the end of the needle will be able to use all the carbon atoms coming into its vicinity and the needle will grow lengthwise toward the source of carbon. If the reverse conditions are true, carbon must flow past the end of the needle and attach itself to the sides of the needle, which then grows in volume mainly by an increase in diameter. If with increasing temperature crystallization velocity grows more rapidly than migratory rate, the sprawliness of nodules should increase with temperature.

A still more rigid treatment would consider also the anisotropic character of graphite, its orientation in space and the effect of radius of curvature of the graphite surface on its solubility.

EFFECTS OF MELTING CONDITIONS ON NUCLEATION OF WHITE CAST IRON

Although it has just been shown that the number of nuclei that are capable of growth to nodules during the graphitization of solid white cast iron is in part dependent upon the temperature at which the graphitization occurs, it will be informative to determine whether melting conditions also may affect this number.

Experiment has shown¹⁷ that the superheating of a white iron melt increases the number of nuclei and, so far as may be judged from inspection of micrographs, renders them more compact. The statement is also made in that connection that an increase in silicon content increases the nodule number. Many students have been attracted by the concept of a nucleus as a vestige of a preexisting graphite crystal. The rate of solution of graphite crystals of the size found in pig iron is such¹⁸ that vestiges may well survive a melting operation.

The present authors can report upon the results of certain experimental melts made in an attempt to learn more of the relation between nucleation and melting time and furnace temperature. In order to eliminate the persistence of graphite crystals the melting stock was chosen from nongraphitic materials, 260 lb. of white iron containing about 2.45 per cent carbon and 0.85 per cent silicon and 4 oz. of 50 per cent ferrosilicon constituting a charge. The second melt to be described contained by inadvertence 1½ lb. of soft iron wire in substitution for an equal weight of hard iron.

The melting was done in a rocking electric furnace. Gas analyses showed that the atmosphere of this furnace contained normally some 29 to 30 per cent CO and the remainder largely nitrogen, there being usually but fractions of 1 per cent of O and CO₂. The white cast iron was melted in the furnace and heated to about 1500° C. When it was quietly molten the ferrosilicon was added and test bars poured at intervals, the temperature being dropped as rapidly as possible to just above 1400° C. and held there as continuously as could be by control of the current input.

Temperatures were measured with a radiation pyrometer sighted on the back wall of the furnace. In the first heat no oxidation of the metal was attempted. Specimens of the forms prescribed by the A.S.T.M. were cast, annealed in a commercial malleable operation and tested. Other specimens broken from unannealed tensile specimens were heated 5 hr. and 15 hr., respectively, in cast-iron borings at 900° C., and the graphite was determined. The number of nodules (larger than $0.02 \pm$ mm. in diameter) was determined for the longer annealing period, though with less precision than in the first reported portion of this investigation because of the much smaller number of nodules per unit volume. The density of graphite packing was calculated as previously described. The data are summarized in Table 3. The data for a second heat similar to the first, in which air was introduced into the furnace at a controlled but not measured rate, are reported in Table 4.

In a melt held in an atmosphere consisting almost entirely of N₂ and CO without important changes of temperature, the composition remained substantially unaltered for over two hours. The number of nodules capable of growth at 900° C. decreased sharply between 20 min. and

44 min. after beginning the experiment and the sprawliness of the nodules increased. The graphitizing rate, however, remained approximately constant throughout. This points to a more rapid deposition of graphite per unit area of nodule-metal interface for metal held molten a longer time, which should favor sprawliness.

The poor tensile strength and elongation, especially marked at the end of the heat, is interesting but forms no part of our major subject. In the second heat we note for comparison a slow decrease in tensile

TABLE 3.—*First Malleable Heat*

			Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7	Bar 8	Bar 9	Bar 10
Pouring time after silicon addition, min			3	17	20	36	44	63	84	102	123	133
Oxidising heat-treatment, min			None	None	None	None	None	None	None	None	None	None
Pouring temp., deg. C			1470	1460	1410	1410	1405	1410	1405	1410	1425	1415
Carbon content, per cent .			2.48				2.39				2.35	
Silicon content, per cent			0.89				0.87				0.90	
Tensile strength, lb. per sq in.			47,750	44,200	46,000	47,650	46,100	46,800	47,800	46,800	43,750	43,300
Elongation in 2 in., per cent			11.5	5.5	9.0	9.5	9.0	8.0	9.0	8.0	5.5	5.0
Heat-treatment at 900° C.	5 hr.	Graphite, per cent	0.14	0.17	0.15	0.13	0.14	0.15	0.19	0.14	0.17	0.25
	15 hr.	Graphite, per cent.	1.00	0.84	0.90	0.87	0.85	0.76	0.79	1.01	1.05	1.15
		Nodules per cu. mm.	98.0		111.2		45.1		41.6		50.3	
		Density of graphite, nodules	0.37		0.36		0.57		0.74		0.73	

strength with time and falling temperature up to the moment when air was introduced, then a sharp increase in tensile strength and elongation occurred.

The nuclei number first decreased with time and temperature until air was admitted and then increased to the initial value, the sprawliness remaining constant. The graphitizing rate as measured by the deposition of graphite in 5 hr. at 900° C. increased somewhat when air was first admitted but otherwise remained approximately constant. The deposition in 25 hr. has gone too near completion to serve as a satisfactory measure of graphitizing rate.

That the addition of air has a permanent effect on the bath is evidenced by the persistence of lowered CO concentration. The samples were removed while the air was not flowing and it would seem that the

TABLE 4.—*Second Malleable Heat*

			Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7
Pouring time after silicon addition, min			8	14	17	32	64	91	109
Oxidizing heat-treatment, min.			None	None	None	None	4	6½	4¾
Pouring temp., deg. C. .			1510	1500	1415	1405	1415	1425	1480
Carbon content, per cent			2 47			2 45			
Silicon content, per cent..			0 93			0.91			0 96
Carbon monoxide in fur- nace gas, per cent			32			29 4	27.4		27.5 ^a
Tensile strength, lb. per sq. in.			50,000	50,400	50,500	47,700	52,800	53,300	54,900
Elongation in 2 in., per cent.			8 5	9 5	10.0	7.0	14.5	13.0	16 0
Heat treatment at 900° C.	5 hr.	Graphite, per cent..	0 52	0 45	0 69	0.62	0.78	0.94	0.79
	25 hr.	Graphite, per cent..	1 35	1.18	1.24	1.32	1.32	1 27	1 20
		Nodules per cu. mm. . .	64.6	42.1	41.1	40 0	45.4	55 7	62.9
		Density of graphite, nodules .	0 36	0.56	0 51	0 54	0.50	0.51	0.53

^a 23.2 per cent CO last analysis 8 min. later.

incandescent electrodes could furnish ample opportunity for the very rapid re-establishment of gas equilibrium.

Comparing these experimental melts with the air-furnace metal described in the previous section, a vast difference, of the order of 10 to 1, is observed in the number of nodules (of significant size). By the usual methods¹ it can be shown also that at 900° C. the time required to pre-

precipitate one-half the available carbon of graphite is about $1\frac{1}{2}$ hr. in the air-furnace metal, 10 to 15 hr. in the heat described in Table 3 and from 4 to 6 hr. in the heat of Table 4, depending on whether or not air was available.

It has been reported¹⁹ that metal melted in a similar furnace, without air, and at much higher temperature, may contain very high silicon contents without primary graphitization, and such iron is shown to contain fine temper carbon nodules. The graphitizing rate was rapid but an allowance must be made here, as also for the air-furnace metal, for an increased silicon content. No data are given suitable for quantitative evaluation.

Tables 1 and 2 may be considered to exemplify the conclusions that in graphite-free melts* reducing conditions decrease the number of nuclei and moderate oxidizing conditions increase them, and that the oxidizing increases the subsequent graphitizing rate to a very limited degree.

NUCLEI DEVELOPED DURING FREEZING OF GRAPHITIC IRONS

The number of nuclei from which mottles develop can be studied in precisely the same manner as the growth of temper carbon nodules. When the growth of graphite reaches the stage at which adjacent mottles coalesce completely the iron becomes gray, all trace of the identity of individual mottles is lost, and the possibility of recognizing how many nuclei originally participated in the graphitizing process no longer exists. So long as individual mottles are recognizable we may still proceed, as with temper carbon nodules, to determine the percentage of the aggregate volume of these mottles that is occupied by graphite, and use this as a measure of the "sprawliness" of the graphite. When the mottles have completely merged, however,† the aggregate volume of the mottles is evidently the total volume of the metal and the number that serves so well to measure the "sprawliness" of nodules becomes merely the volume percentage of graphite in the cast iron and in no way measures any characteristic of the graphite's geometrical distribution.

In an attempt to evolve some other method of evaluating numerically the distribution of graphite in space so as to have quantitative means of designating coarseness and fineness, the expedient was adopted of observing the frequency with which random straight lines drawn across the section intersected graphite flakes. This constant is designated as

* We cannot, of course, say that the white iron of the charge does not graphitize to some extent just before melting.

† There is no analogy for this condition during graphitization in the solid state, for nodules never touch each other.

the flake number per millimeter. The experimental procedure was as follows.

Carefully prepared metallographic specimens were examined at 200 dia. to find the area in a given mottle (or what had been a mottle before coalescing) in which the graphite flakes were most thickly packed.* This area magnified 2000 dia. was projected upon a screen ruled in squares 1 cm. on a side and the number of intersections per unit of length was counted, using usually a ruling 10 cm. square and therefore containing lines of an aggregate length of 22 centimeters.

To exemplify and supplement earlier information⁷ that in mottled irons nucleus number is related to chemical composition, oxidizing conditions during melting, and cooling rate, three experimental melts were made by methods closely analogous to those already described. In only one of these could nucleus number be followed satisfactorily.

In order to exclude vestigial graphite as a cause of nucleation as much as possible, the melts were made from graphite-free material. The first of the three consisted of 245 lb. of sprue (2.45 per cent C, 0.85 per cent Si), 55 lb. of washed metal (3.75 per cent C, 0.0 Si) and 6 lb. 2 oz. of 50 per cent ferrosilicon; the second of 248 lb. of sprue, 12 lb. of washed metal and 6 lb. 7 oz. of ferrosilicon; the last of 253 lb. of sprue and 7 lb. 7 oz. of ferrosilicon.

The melting operation, in general, was conducted much as described for the malleable heats. Test specimens were $1\frac{1}{4}$ in. in diameter, molded in green sand, on end, and tested on supports 12 in. apart. Tensile specimens were machined from the broken ends unless the metal contained blowholes or was too hard. Tables 5, 6 and 7 give the resulting data. In each case the ferrosilicon was added after the remainder of the charge was melted and brought to temperature.

Since our major interest is in nucleation, we may center our attention mainly on Table 7. An actual evaluation of the number of nuclei per unit volume proved impossible, owing to metallographic difficulties in measuring the intercepts of mottles with a plane surface, especially when the mottles are so small as to require examination under the microscope but so large that a considerable area must be photographed to obtain a random plane. Being unable to overcome these difficulties, we had to content ourselves with an approximation of the average size of intercept instead of a statistical distribution by sizes. It appears, however, that the average size of mottle increased for the first 100 min. and the number per unit area decreased. The qualitative conclusion is inescapable that the mottles increase in size and decrease in number to a roughly constant minimum value under the existing conditions. It

* It may be argued that instead of choosing the densest areas an average over an entire mottle should have been used.

follows that the number of nuclei approaches a minimum (under reducing conditions).

The amount of graphite formed (in the 1¼-in. dia. specimens) during cooling seems to decrease and then increase. This phenomenon may well be ascribed to the composite effect of a decrease in number of nuclei and an increase in crystallization velocity. There is also a corresponding change in the property we have called "sprawliness," which reaches a maximum when the amount of graphite formed during cooling is a minimum. From Tables 5 and 6 we learn nothing regarding nucleation but observe what seem to be random changes in sprawliness. We point, however, to the very slow changes in combined carbon in these two tables, as evidence that graphitizing rate during freezing was but little affected by the changing melting and pouring conditions recorded here.

EFFECT OF GRAPHITE DISTRIBUTION ON PHYSICAL PROPERTIES

Although the primary concern of this paper is with nucleation, the relation of this variable to physical properties should not be overlooked.

TABLE 5.—*First Gray-iron Heat*

	Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7
Pouring time after silicon addition, min . . .	5	17	35	46	63	74	92
Oxidizing heat treatment, min	None	1	3	3*	2	6	2*
Pouring temp, deg C° . .	1490	1430	1365	1355	1310	1325	1330
Carbon content, per cent	2.76				2.69		2.72
Silicon content, per cent	1.82				1.77		1.76
Fracture	White edge, gray center	Gray	Gray	Gray	Gray	Gas holes gray	Gas holes gray
Flakes per mm . . .	77.2	99.2	100.0	56.8	46.8	53.2	79.6
Transverse load, lb per sq in	3,445	3,955	3,465	3,790	3,390	3,575	2,825
Tensile strength, lb per sq in			38,100	31,400	28,200		
Combined carbon, per cent	1.42	1.25	1.17	1.17	1.21	1.25	1.29

* Blown in while arc was on.

The malleable heat described in Table 3 has surprisingly poor physical properties, which deteriorate with time, whereas the properties shown in Table 4 are fair up to the introduction of air and then improve decidedly. The composition of the two heats and the pouring temperatures are substantially alike.

The density of the graphite nodules does not alter sufficiently in Table 3, nor in the right direction, to account for any marked change in physical properties, nor is the distribution of sizes in the more completely graphitized specimen of Table 4 significantly different for the several specimens.

TABLE 6.—*Second Gray-iron Heat*

	Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7	Bar 8	Bar 9	Bar 10
Pouring time after silicon addition, min	15	19	34	39	54	59	71	79	91	104
Oxidizing heat- treatment, min .	None	None	None	None	4	None	3½	None	3½	3½
Pouring temp., deg. C.*	1445	1510	1405	1480	1395	1495	1370	1495	1425	1405
Carbon content, per cent		2 71			2 66				2 63	
Silicon content, per cent		1 81			1 89				1 90	
Carbon monoxide in furnace gas, per cent	29 6	28 0			23 2		24 0		21 7	24 7
Fracture	Almost all gray ^b	Light gray ^c	Gray	Gray	Gray	Gray	Gray	Gray	Gas holes gray	Gray
Flakes per mm	67 2	54 6	48 6	48 6	88 6	84 6	39 0	109 6	180 4	83 6
Transverse load, lb. per sq in	4,125	4,700	4,890	4,600	5,140	4,860	5,145	4,760	3,055	3,820
Tensile strength, lb. per sq in		49,700	52,300	45,600	47,700	50,200	56,000	55,800		
Combined carbon, per cent	1 17	1 17	1 17	1 25	1 17	1 15	1 17	1 09	1 05	1 01

* Note the variety of pouring temperatures.

^b Unmachinable.

^c Very bad machinability.

The increase in graphitizing rate with time shown in Table 4 confirms the increase in nodule number. The differences in physical properties do not seem to be explicable from the viewpoint of graphite distribution, and some other explanation not touched upon in the present study would seem to be needed for the observed facts.

Tables 5, 6 and 7 point clearly to the fact that it is not sufficient merely to decrease the total carbon in order to increase the physical properties of cast iron. Comparing Table 5 with Table 6, we observe in

general that the stronger heat is rather definitely lower in combined carbon, both series apparently being hypereutectoid. A relation between graphite, combined carbon and tensile strength showing the great importance of the former has been published elsewhere.²⁰ Perhaps one may see such a relation also throughout Table 6. In Table 7 we observe first a decrease and then an increase in combined carbon for which no analog is seen in the transverse-load data.

TABLE 7.—*Third Gray-iron Heat*

	Bar 1	Bar 2	Bar 3	Bar 4	Bar 5	Bar 6	Bar 7	Bar 8	Bar 9	Bar 10
Pouring time after silicon addition, min .	14	43	59	75	93	110	130	146	166	186
Oxidising heat-treatment, min	None	None	None	None	None	None	None	None	None	None
Pouring temp., deg. C °	1395	1390	1390	1395	1405	1405	1405	1415	1390	1415
Carbon content, per cent		2 37		2 38				2 34		2 30
Silicon content, per cent		2 33		2 23				2 14		2 12
Carbon monoxide in furnace gas, per cent		31 3		28 3		27 7		28 3		24 5
Fracture .. .	75% gray 25% white	Almost gray	Gray	Gray	Gray	Mottled	Mottled	Mottled, almost gray	Badly mottled	Mottled
Average mottle diameter, mm ^b	0 35	0 425	0 50	0 575	0 65	0 80	0 80	0 80	0 70	0 80
Average mottles per sq. mm ^c	7	7	6	5	3	0 47	0 24		0 72	0 53
Flakes per mm ..	73	101	97	130	125	201	155	167	175	176
Transverse load, lb per sq. in	3,310	3,775	4,010	3,920	3,270	4,045	3,780	3,910	4,315	3,650
Combined carbon, per cent	1 33	1 42	1 17	1 01	0 89	♣	♣	1 05	1 33	♣

° Readings ½ or 1½ minutes before pouring

^b Approximately.

^c Nos. 1 to 5 approximately, the others counted.

♣ Unmachinable

The lack of correlation between physical properties and any measurable characteristics of the graphite content and form is possibly to be interpreted rather as evidence of the highly complex character of the relation between the many variables than of a complete lack of relationship. The very superficial survey recorded here may be useful mainly as a guide to the many variables that require control in any investigation attempting to correlate the physical properties with any single variable.

DISCUSSION OF OBSERVATIONS

The investigation, coupled with previously existing knowledge, leads to certain generalizations with regard to nucleation in hypoeutectic cast irons.

In the white cast irons at least the number of nuclei per unit volume that can be recognized is not determined by the melting and freezing conditions alone, but also by the temperature at which the nuclei are caused to grow. In general, the observed nodules fall in such metal into two very diverse groups as to size. One sort of nodule never grows to any considerable size, the other does. The former type is numerous, perhaps 10 to 20 times as frequent as the latter, but the individuals are so small that their aggregate graphite content is negligible. These small nodules appear to increase in number with time at graphitizing temperature but this may be an illusion and due to an increased visibility with increasing size. Such finely divided temper carbon has been held²¹ to be evidence of the stable iron-carbon eutectoid, but for the authors' material quenched from 900° C. this explanation is not applicable.

The larger nodules do not alter greatly in number with time but do change in size. This constancy of number, in the first approximation, represents in part something approaching a balance between a low birth rate of nodules and a slow coalescence under surface-tension forces. At any given time the size distribution of nodules is not very wide, most of them falling into a rather narrow range of diameters. Even very early in secondary graphitization a few nodules have grown to practically their maximum size, but the great majority remain of nearly uniform size, which increases with time.

The number of the larger nodules certainly, and perhaps also the number of the smaller ones, decreases as the graphitizing temperature decreases, and hence, also, in a given iron the maximum size attained by nodules increases. By size of nodule here is meant the size of the circumscribing sphere. The density of graphite packing in these spheres decreases as the graphitizing temperature increases. It is, however, remarkably constant at a given temperature.

On the other hand, the number of nodules is not solely a function of the graphitizing temperature, for there is a profound difference in numbers of the larger type between the two experimental heats described and the air-furnace metal upon which our data as to the growth of nodules are based. There is some ground for considering this to be perhaps an effect of graphite spores remaining from the pig iron of the air-furnace charge. Even in our heats there may have been a little vestigial graphite remaining from carbon liberated while the sprue was heated to the melting point. At any rate, we observe a distinct decrease in nodule

number with time in Table 3, which should be evidence of the elimination of nuclei with time. These nuclei, however, may be merely oxides that are being removed either by reduction or flotation. The latter viewpoint receives confirmation not only by the improbability that much graphite could have formed during melting but also by the increase in nodules observed in Table 14 when air was introduced into the furnace. The magnitude of this effect as compared with the difference between the experimental and commercial metal suggests that vestigial nuclei are of great importance in determining the number of nuclei that will grow into nodules. Commercial practice confirms this conclusion indirectly, for there is commonly considered to be a connection between the pig-iron content of a heat and annealability. Even in a given metal graphitized at a given temperature it is known^{21,22} that graphitizing rate is enormously increased by previous quenching of white cast iron from about 1000° C. Such a treatment produces an enormous increase in nodule number.

A change in graphitizing rate with nucleus number is qualitatively visible in Table 4.

Since the distance between nuclei is inversely proportional to the cube root of the number per unit volume, the migratory paths for carbon in the air-furnace iron are of the order of magnitude of $\sqrt[3]{\frac{60}{500}}$ or about one-half as long as those in the electrically melted metal. The time to attain one-half completion in graphitization is, however, between $\frac{1.5}{15}$

and $\frac{1.5}{4}$ times as great. This and the difference in graphitizing rate between the two electric-furnace heats that are at least comparable in nucleus number suggests differences in migratory velocity with changes in chemical composition and melting history. Even in the same heat, Table 3, the rate of graphitization does not vary materially or systematically with considerable changes in the number of nuclei upon which carbon is deposited.

These observations point toward the suggestion that nucleus number is an important factor, but not the only one, in the determination of graphitizing rate. "Sprawliness" may play a part here, for the migratory distance to the nearest graphite will decrease as the "sprawliness" increases. "Sprawliness," though roughly constant with time in a given iron at a given temperature, varies with different irons. The two electric-furnace irons are similar in this respect but show a density of graphite packing in the nodule about three times as great as does the air-furnace iron, all at 900° C.

The number of nuclei capable of growing into mottles during the freezing of cast iron is plainly much smaller than the number that can grow into nodules on subsequent heat-treatment. This is qualitatively confirmed by the commercial observation that if a mottled iron is

graphitized the flaky carbon of the mottles remains visible, mapping out a coarse pattern of mottles among a much finer distribution of temper carbon nodules.

It appears that the nuclei for mottle formation disappear with time in liquid metal or else are rendered incapable of growth by such prolonged holding. The former seems the simpler assumption.

So far as may be judged from the number of mottles intersected per unit area of the metallographic plane, the average number of nodules is of the same order of magnitude in all the gray-iron heats, except toward the end of that described in Table 7, where no oxidation was employed. A simple explanation might be that the nuclei are oxides tending to be removed by the reducing action of the carbon of the metal, which are reformed in the presence of an oxidizing atmosphere. That vestigial nuclei of graphite remain is very probable.

The boundary of atmospheric composition between the two reactions is roughly at 25 per cent CO in a gas that originally was air. Since CO occupies twice the volume of oxygen used in its formation, the air from which these furnace gases are formed occupied 87.5 per cent of the volume of the gas. Its oxygen content by volume was one-half the CO content of the furnace gas plus the CO₂ content of the latter, and this oxygen content was 20.9 per cent by volume of the original air; hence the CO₂ content of the furnace gas should have been about 5.8 per cent and the CO content of the mixture of CO and CO₂ is about 81 per cent (independent of pressure) which is close to the equilibrium value for the system Fe-FeO,²³ at least in the solid state. This is at least suggestive of the role of FeO in nucleation. It has been suggested by others²⁴ that ferrous silicates in a finely divided slime or colloidal suspension are the actual cause of nucleation.

The nuclei that grow into mottles during the freezing process are enormously less numerous than those that can grow into nodules on secondary graphitization. A mere temperature effect would seem to require an increase rather than a decrease in number. An increased number of nuclei in white iron as compared with mottled iron may well be ascribed to increased supercooling. The supercooling in the white areas of mottled irons is greater than in the mottles, thus accounting for the great numbers of nodules that can be grown in these areas by subsequent secondary graphitization. The decrease in nucleus number shown in the last gray-iron heat as the metal progressed from gray to mottled need not constitute an exception to this rule, for another explanation has already been given.

CONCLUSIONS

We have attempted to point out the bearing of certain of our observations on the problem of the growth of graphite from nuclei. It appears all but impossible to condense that summary into a few concrete conclusions.

We have not learned what constitutes a nucleus. It may be a sub-microscopic fragment of graphite¹⁸ or of a metallic oxide or silicate, or only a field of force due to surface tension at an interface.¹¹ We think it may be any one or more of these even in the same metal.

We know experimentally that the number of nuclei that will grow into nodules or mottles is a function of the materials of the charge as well as of chemical composition, and also of the composition atmosphere of the melting furnace and the melting and pouring temperature. It depends, further, upon the rate of cooling during and after freezing, with the accompanying changes in the degree of supercooling, and, lastly, upon the temperature of germination of the graphite.

In the presence of so many variables it is impossible to draw conclusions extending beyond the scope of our experiments and the records in the literature.

ACKNOWLEDGMENT

We are indebted to Messrs. H. H. Johnson, C. H. Junge and George Kunz for much experimental assistance.

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DISCUSSION

(R. F. Harrington presiding)

R. H. SWEETSER,* New York, N Y—This paper seems to fit in with the work that is being done by the Committee on Properties of Pig Iron, of the Iron and Steel Division, and it seems to fit in with what I have learned recently regarding the characteristics that are imparted to pig iron by the kind of fuel that is used in making that pig iron.

H. A. SCHWARTZ—What we thought we knew at one time—I don't know whether this method of examination is right, but like Topsy it just grew—was that if we examined pig iron at the corner of a chilled pig, where the top surface contacts with the mold, never going more than a centimeter from the surface of the chill mold, we may have a form of graphite, which suggests that it is the decomposition product of the metastable eutectic, that is, the mossy form of graphite or, as the German calls it, *grunpeliger grafite*. The iron melted from that is always good from the annealing viewpoint. If from the area, which implies all it should imply, with the same cooling, the flakes of graphite are very coarse, the iron may be difficult to anneal, although it is not always difficult to anneal. That cannot be a question of the actual form of graphite flake, because the pig iron that has the decomposition form of graphite in the chilled zone still has very coarse graphite in the middle of the pig. It is not the mere fact that there are some large graphite flakes, and that large flakes give some undesirable property. We should be very glad of any attempt to find out why one of these things happens rather than the other.

I want to emphasize that all coarse graphite pig iron is not necessarily troublesome. No pig iron that has this finely divided kind of graphite in this particular location has

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ever been troublesome. The coarse kind makes many heats in which nothing unusual happens. There are certainly many more steps in the problem than the very simple one I have outlined. That is another aspect of what makes nuclei, by the way.

T. L. JOSEPH,* Minneapolis, Minn.—What is the relative importance of oxide inclusions in this picture? A number of things are acting. At the present time do you think oxides play an important part as nuclei for graphite?

H. A. SCHWARTZ.—I know sulfides do, and I presume oxides might. In fact, we hope soon to have a picture of temper carbon growing around sulfides. One of our investigators is wondering whether it is only an interface as such that forms crystallization, or whether the nucleus has to have some crystallographic similarity to the thing growing on it.

It seems to be accepted by most people that if temper carbon is grown on many crystals the rate of graphitization is first helped. The properties also are helped. I do not know whether anybody has formally proved it as to properties. The graphitizing rate has been proved

J. S. VANICK,† New York, N Y—I am thinking of the relation between annealing rates and nuclei count for the reduced metal conditions in the electric furnace as against those in the open-flame furnace. Evidently the open-flame furnace speeded up graphite formation, rather indicating that perhaps a certain amount of oxygen is a desirable thing. That is one feature that you have probably developed at greater length than is indicated in your summary.

Another point is that you have used white iron charging stock, presumably free of graphite. Then the question arises: What would happen if you used the same composition, carrying graphite in the charging stock, and worked it the same way without superheating? Then comes the superheat question, of course. I am not sure that there might not be one or two others

H. A. SCHWARTZ—We particularly omitted the graphite problem because of those very complications; not that it is not interesting, but we had to stop somewhere in the time Dr. Ruff had at his disposal in this country.

The question of atmosphere is, in fact, dealt with somewhat further in the original paper. The traditional idea is that oxidation interferes with the graphitization rate. If you reached the last degree of eliminating oxidation, that might not be at all so

F. L. WOLF,‡ Mansfield, Ohio.—What about the question of agitation?

H. A. SCHWARTZ.—We did not agitate except for the rather gentle rocking of the furnace.

J. S. VANICK—Have you developed, in connection with nuclei formation at an interface, the origin of nuclei well enough to be able to say whether they occur, say, in the centers of the austenitic cells, or sprouting out in the labyrinth of meshes in this hypereutectic iron?

H. A. SCHWARTZ.—Metallographically, there does not occur what you think ought to occur in the white iron. There are more needles of cementite than seems reasonable. I think all the temper dots in the white iron appear between the cementite and the austenite at the time they first appear. That was first suggested by Allen, of the American Brake Shoe, and we have since checked it in several different ways.

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‡ Chemical Engineer and Technical Superintendent, The Ohio Brass Co.

When such interfaces exist, they are predominant determiners of where these nuclei come in; when they do not exist, something else has to take their place, and that might be sulfides.

If there is carbon in the mass, the carbon granule itself is the predominant determiner of where the other carbon is to go. Sometimes photomicrographs show sprawly flakes of graphite on which warts have grown, showing secondary graphitization. The complexity of the whole problem is so great that some factors must be excluded experimentally so that the effect may be observed of variables to which the system is less sensitive.

J. S. VANICK.—Would the nuclei forming at the interfaces be the ones that grow to a large size?

H. A. SCHWARTZ —Yes. The small ones are very erratic at the present time

T. L. JOSEPH —Is there any physical property, like hardness, that gives an index of the state of the graphite, the nodular graphite and the flaky?

H. A. SCHWARTZ —It would be very crude. I do not think we could depend on it. The statistical treatment is terribly laborious. It is a great strain on one's eyes to measure the diameters of a few thousand nodules. The actual areas we have measured for each one of these experiments were 10 in. wide and 1 ft. long in the photomicrographs at about 300 diameters. That is tiring work.

Surface Magnetization and Block Structure of Ferrite*

BY W. C. ELMORE† AND L. W. MCKEEHAN‡

(New York Meeting, February, 1936)

THE magnetic powder method, long used for roughly mapping magnetic fields, has recently been refined^{1,2} for investigating the microscopic variations in the surface magnetization of ferromagnetic crystals. Bitter² first discovered regular powder patterns connected with the crystal structure of such specimens. Several other investigators³ have used Bitter's original technique, with slight modifications, to study the variation of the patterns with variations in the magnetizing field applied parallel to the surface, and their dependence upon the state of strain, of polish and of crystal cut. All of the explanations of these patterns on metallic ferromagnetics have been couched in general terms. In a preliminary report we have described an improvement in the powder technique which led us to the discovery of a new effect throwing considerable light on the magnetic secondary structure of alpha iron⁴ and of nickel⁵ single crystals. We now report additional evidence confirming the existence and stability of a magnetic block secondary structure.

SPECIMENS

The following list describes the specimens used in the present investigation.

DESIGNATION	DESCRIPTION
A ₁	Silicon ferrite furnished to us by Dr. W. E. Ruder, of the General Electric Co., for which he gave the following typical analysis: C, 0.05; P, 0.038; S, 0.026; Mn, 0.15; Si, 3.24. Disk, 0.60 cm. diameter, about 0.05 cm. thick. By X-ray analysis angles between disk normal and [100] 75°, [010] 76° [001] 21°.
A ₂	Same as A ₁ except: diameter 0.75 cm.
A ₃	Same as A ₁ except: diameter 0.68 cm.

* Condensed from a dissertation submitted by W. C. Elmore in candidacy for the degree of Doctor of Philosophy. Manuscript received at the office of the Institute Aug. 5, 1935.

† Yale University.

‡ Professor of Physics and Director of the Sloane Physics Laboratory, Yale University, New Haven, Conn.

¹ References are at the end of the paper.

DESIGNATION	DESCRIPTION
B	Same as A ₁ except: polygonal piece a few millimeters on each edge with angles between normal and [100] 76°, [010] 73°, [001] 22°.
C	Same as B except: angles between normal and [100] 87°, [010] 56°, [001] 35°.
D	Same as A ₁ except: diameter 1.33 cm, thickness 0.022 cm. This specimen is No. 1 of R. F. Clash and F. J. Beck ⁴ , who used it in studies on the directional distribution of Barkhausen changes in magnetization.
E	Ferrite furnished to us by Dr. D. D. Foster, of the Bell Telephone Laboratories, for which he gave the following analysis (before wire-drawing operations): C, 0.02; P, 0.012; S, 0.005; Mg, 0.01; Al, 0.36; Si, 0.008; Cu, 0.04; Pb, 0.02. Wire 1 mm. in diameter. Angles between axis of wire and [100] 82°, [010] 68°, [001] 24°.
F	Silicon ferrite furnished to us by N. P. Goss, Cold Metal Process Co. Several pieces cut from a strip about 0.033 cm. thick, including a disk used by Clash and Beck ⁴ .

POLISHING

The polishing procedure finally adopted was one that minimized surface strains. Each of the usual polishing steps was continued about twice as long as it took for the scratches from the previous step to disappear as judged by the unaided eye. The final polish was done on a horizontal rotating disk covered with wool broadcloth impregnated with a paste of c.p. magnesium oxide (Merck) in water.

DEPOSITION OF COLLOID

The colloid was prepared by grinding gamma (ferromagnetic) Fe_2O_3 to submicroscopic size in a porcelain ball mill containing water and a little gum arabic. It was furnished to us by Dr. L. A. Welo, of Tottenville, Staten Island. The individual particles, in violent Brownian movement, could just be seen at high magnification with dark field illumination. A few drops of colloid were placed on the polished surface of the magnetized specimen. After a few minutes, a cover glass was placed over the specimen, squeezing the liquid to a thin layer. The cover glass was held from touching the specimen by mounting the specimen in a shallow well, or by putting a few bits of wax near the edges of the cover glass.

The specimens were always magnetized by mounting on the pole of a small vertical electromagnet, previously described⁴. In one experiment the specimen, firmly attached to the pole of this magnet, was mounted in the horizontal field of a larger (du Bois) electromagnet. This arrangement permitted independent control of the normal and transverse magnetizing fields. The patterns were observed with a microscope employing vertical illumination; an 8-mm. objective proved to be most useful.

To prevent the colloid from attaching itself to the specimen, it was found necessary to leave an invisible film of grease on the polished surface.

If the surface was washed with CCl_4 , the colloid tended to stick fast, while if a protective coat of grease was merely wiped off with cotton, this sticking did not occur. The tendency of the colloid to form rust on some iron crystals was reduced by adding a small amount of KOH to it. Owing to the deleterious coagulating effect of KOH, this procedure was later discarded in favor of copper-plating the carefully cleaned surface. A cyanide bath was used. The thin layer of copper did not interfere with the formation of patterns⁷, but was used only when necessary.

RESULTS

We previously reported⁴ a characteristic shifting of the colloid lines on silicon ferrite crystals upon reversal of the normal magnetizing field. With no field a pattern appeared comprising both sets of lines, spaced about 2μ . Fig. 1 shows highly magnified the three patterns on a polished face not much inclined to a $\{100\}$ plane. To explain these patterns we imagined the surface to be composed of small blocks, 2μ on an edge, magnetized parallel to the surface along axes of form $\langle 100 \rangle$ and $\langle 110 \rangle$. The magnetization of these blocks opposes at half the boundaries, so that the net magnetization is as small as possible over any region. We discussed the manner in which this model accounted for the three observed patterns and the shift from one pattern to another. The blocks (possibly cubes), or perhaps groups of them, may be tentatively identified with the domains of the Heisenberg-Weiss theory of ferromagnetism⁸.

PATTERNS WITH LARGER SPACING

We now report and discuss further results obtained with silicon ferrite crystals. Fig. 2 shows three patterns obtained on A_2 . Instead of the usual nonpreferential polish with MgO paste, this specimen was given a preferential polish with alundum, the direction of polishing strokes being evident from the fine scratches, which show best in the no-field pattern. The majority of the lines with applied field are perpendicular to the polishing direction and are spaced about 12μ . The other set of lines, many of which appear split, occur only where parallel sets of the first lines fail to match up. A fine structure is apparent between the prominent lines, as is shown more clearly in Fig. 3, taken at higher magnification.

Additional nonpreferential polish with MgO yielded the usual fine scale pattern. Fig. 4 shows a pattern taken before return to the finer pattern was complete. Although one set of lines is still somewhat more conspicuous than the set at right angles, the average spacing has become 4μ again. The occasional enhancing of lines of the fine pattern disappeared after further polish.

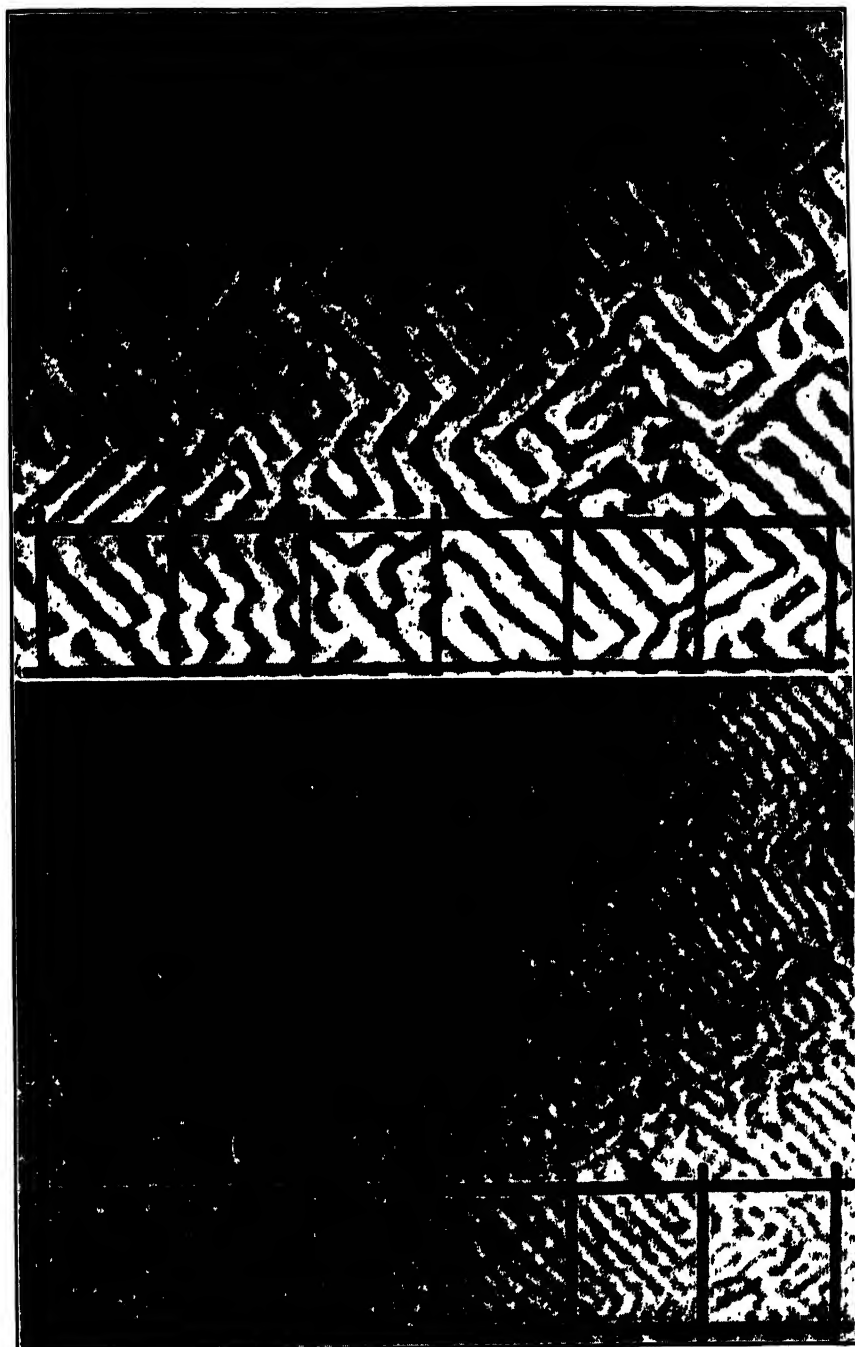
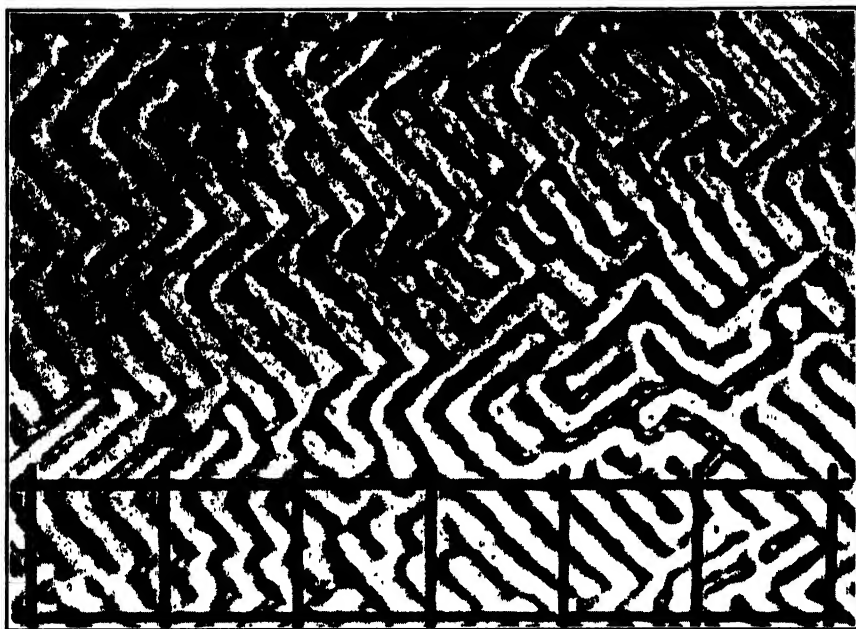


FIG. 1.—SPECIMEN A. GRILLE IS $14\mu \times 82\mu$.
a, normal applied field positive; *b*, zero; *c*, negative.

DISCUSSION OF RESULTS

The block model seems adequate to account for the patterns with larger spacing. We suppose that the direction of magnetization of the 2μ blocks are arranged in sequences of threes opposing, to the depth of several layers, with occasional surface blocks paired off with opposing magnetizations, as indicated in Fig. 5. This scheme gives with normal field dense lines spaced at six block widths, and occasional fainter lines spaced at two block widths, all of which move to unoccupied spaces upon



c
FIG. 1.—(Continued.)

reversing the field. Stray field at the corners of the blocks accounts for the fine structure of dots existing between the lines. With no field the lines of both patterns appear, since there is now stray field at all of the opposing boundaries.

The fine spaced pattern, Fig. 4, still exhibits characteristics of the former pattern. Blocks with magnetizations opposing in sequences of twos are occasionally evident. The enhancement of some of the lines indicates that the arrangements of block magnetizations beneath the surface layer must be contributing excess stray field along particular block boundaries.

That tension will produce magnetic nonuniformities along the direction of easy magnetization most nearly perpendicular to it has been

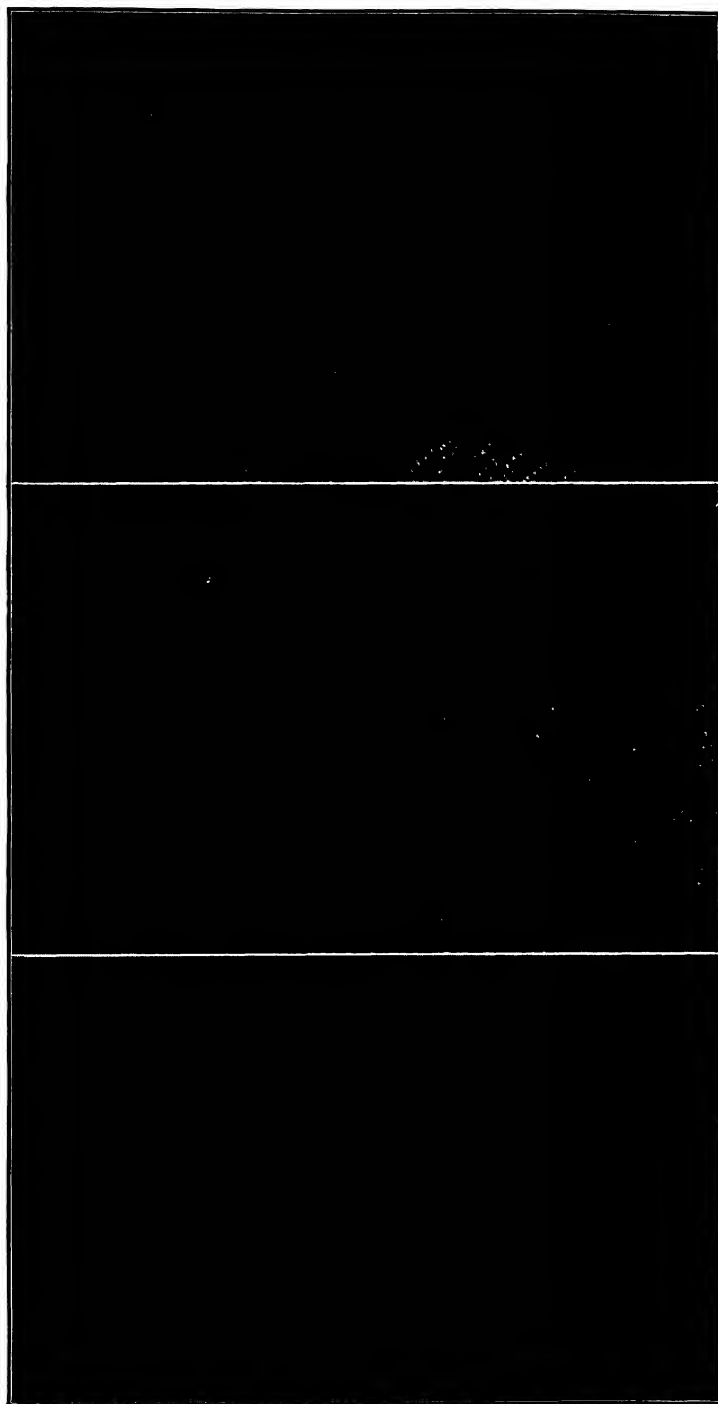


FIG. 2.—SPECIMEN A₂. GRILLE IS $41\mu \times 82\mu$
a, normal applied field positive; b, zero; c, negative.

observed by several investigators, who attribute the effect to magnetostriction. Magnetostriction alone cannot explain why the blocks should arrange themselves opposing in sequences rather than individually. One can speculate that strain may make less marked the difference between

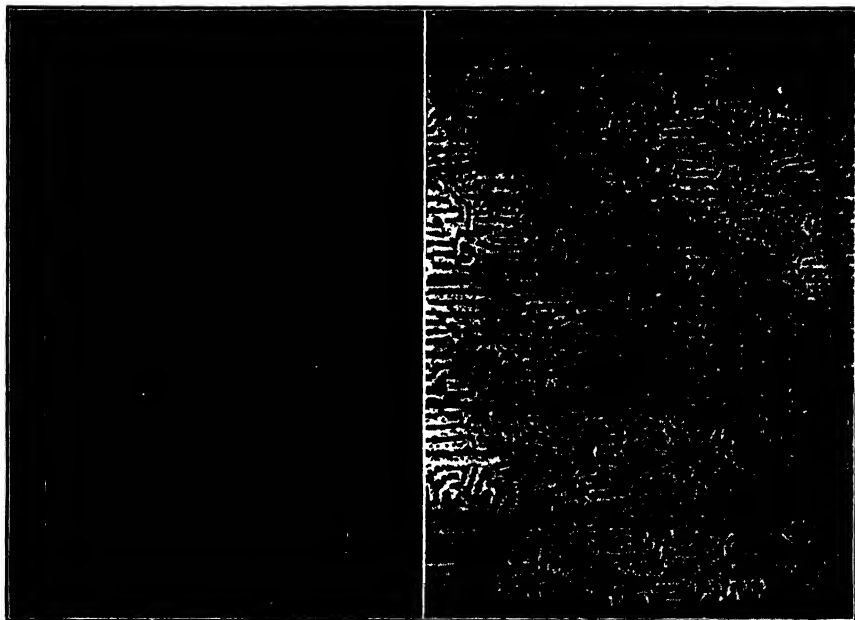


FIG. 3.—SPECIMEN A₂. PROMINENT PARALLEL LINES 12 μ APART.

FIG. 4.—SPECIMEN A₂, AFTER INCOMPLETE REPOLISHING. GRILLE IS 41 μ \times 82 μ .

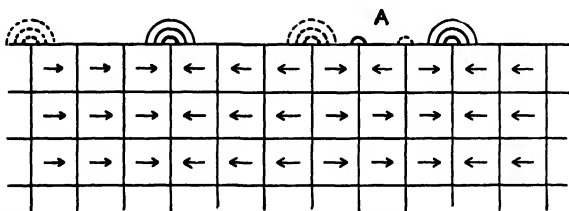


FIG. 5.—SCHEMATIC CROSS SECTION OF A SPECIMEN WITH SEQUENCES OF BLOCKS. Semicircles (full and broken lines) show position of colloid patterns for positive and negative normal applied fields. One surface block (A) is reversed.

boundary planes and block interiors. More energy would then be required for a reversal to occur at a block boundary. The net result would be fewer reversals along any surface direction, yielding larger spacings in the powder patterns with normal applied field.

PATTERNS ON VARIOUS CRYSTAL CUTS

To investigate the third dimension of the blocks a series of patterns with normal field were obtained on various cuts of the Ruder crystals

B and C, and the Foster crystal E. The results for B will be presented in some detail; the results for C and E will be summarized.

Crystal B, its orientation determined by a Laue analysis, was carefully cut into three pieces by vertical section. The top surface and an edge of each piece were polished. Patterns were obtained by suitably mounting the specimens on the upper pole of the small vertical electromagnet.

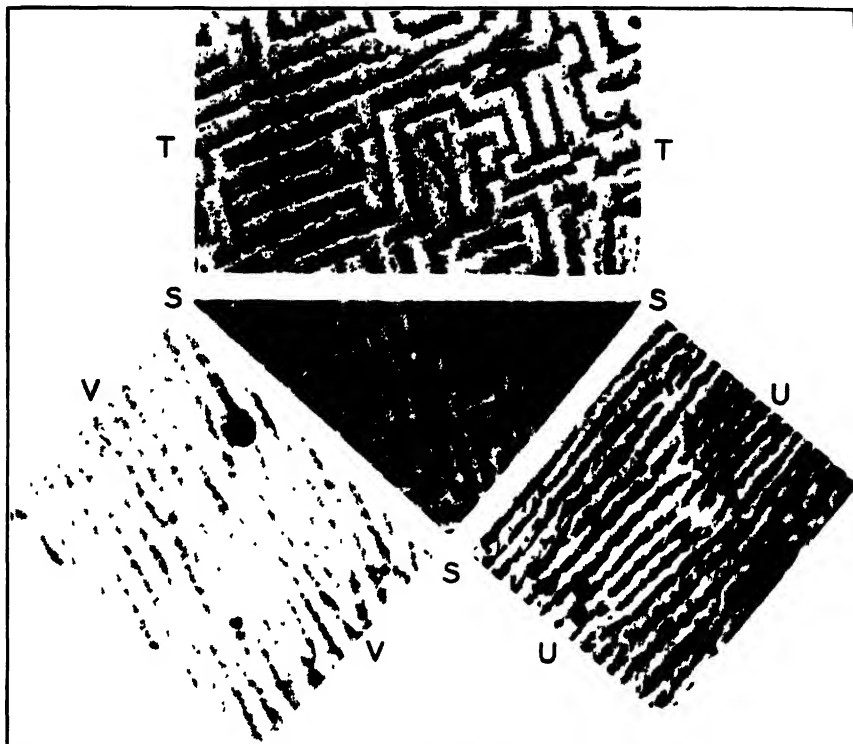


FIG. 6.—SPECIMEN B. PATTERNS ON FOUR CUTS.

Central triangle is that on original surface. The three rectangles are on sections normal to the plane of the triangle and parallel to its adjacent edge. Field applied normal to plane of section.

Fig. 6 shows typical patterns taken on the four different polished surfaces of the three pieces, arranged as if they were the development of the exposed surfaces of one triangular piece of crystal. The stereographic projection, Fig. 7, indicates the position of the cube planes relative to the surface *S*, and the three vertical sections *T*, *U* and *V*.

The average block size was determined, where possible, by counting the number of closely spaced lines per 100μ occurring in several patterns photographed on each of the surfaces. On *T* the block size had to be estimated from the fine structure, since the blocks appeared opposing in

sequences. For the other surfaces, each value in Table 1 represents an average of about 400 line spacings. Individual line spacings varied from the average by as much as 10 per cent.

TABLE 1.—*Block Sizes*

Cut	[100]			[010]			[001]		
	α	D	d	α	D	d	α	D	d
<i>S</i>	14°	5.8 μ	2.7 μ	16°	6.1 μ	2.9 μ	68°		
<i>T</i>	72			17	6 ^a	2.8	9	5.9 μ	2.9 μ
<i>U</i>	51			32			21	5.3	2.5
<i>V</i>	34			56			7	5.0	2.5

^a Estimated.

α = angle between plane of cut and axis indicated at top of column

D = average separation of the closely spaced lines on each cut.

d = average length of block edge $= \frac{D \cos \alpha}{2}$

A similar experiment with the Ruder crystal C yielded a smaller average block size, with the following average dimensions:

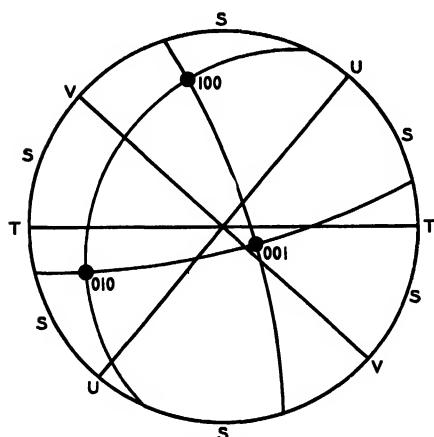


FIG. 7.—STEREOGRAPHIC PROJECTION OF CUTS OF SPECIMEN B.

[100]	[010]	[001]
1.5 μ	1.4 μ	1.4 μ

One of the three vertical cuts approximated a {111} plane, the pattern on which consisted of dots. The tendency of the dots to form lines was not pronounced.

That these results are not peculiar to silicon ferrite crystals was verified by obtaining patterns on two perpendicular surfaces of the more nearly pure ferrite crystal E. The crystal was annealed

in H_2 and then soldered into a hole in a soft iron block, so that one side and one end could be polished. Patterns on these two surfaces gave the following average block dimensions:

[100]	[010]	[001]
2.9 μ	3.1 μ	3.6 μ

These results point to the existence of a magnetic block secondary structure in ferrite crystals. Although the same general polishing

procedure was consistently adhered to, the polishing history of the individual surfaces must have varied considerably. The agreement of the block dimensions found on several cuts of the same crystal strongly indicates that polishing does not influence the observed block size, and hence that the pattern appearing on a given surface is the result of a structure already existing in the iron crystal. That this structure is common to most iron crystals is suggested by the mazelike patterns found on iron by various other investigators.

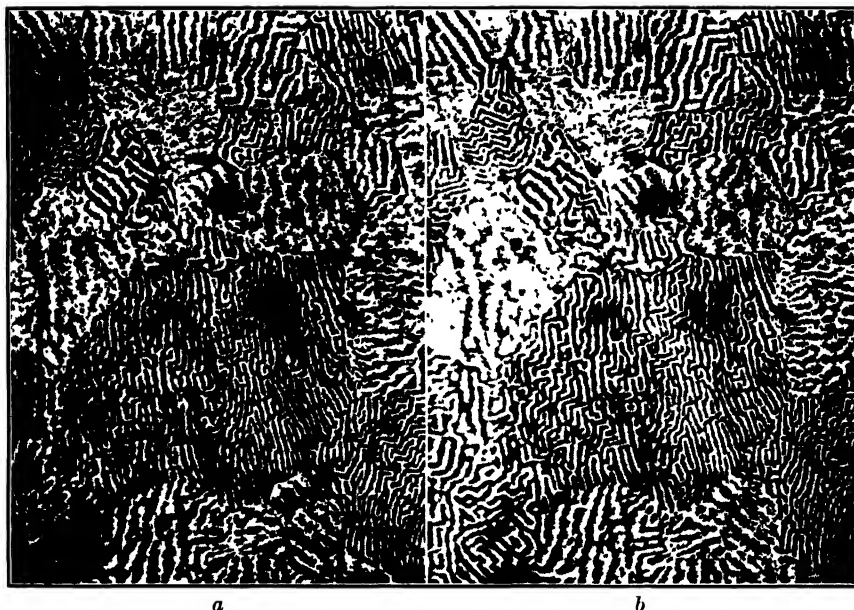


FIG. 8.—SPECIMEN F. DIRECTION OF ROLLING VERTICAL. REGION SHOWN IS ABOUT $460\mu \times 350\mu$.
a, normal applied field positive; *b*, negative.

The size of the block varies from specimen to specimen. Pattern lines have been observed as close as 1μ , which would require a block 0.5μ on an edge, while the maze patterns previously shown by others would require much larger blocks. Of course it is not clear whether these patterns with larger spacings are, or are not, the result of an arrangement of blocks in sequence opposing. Patterns on polycrystalline specimens (Fig. 8) show a considerable variety of spacings in adjacent crystallites, which presumably differ very little except in orientation. Any considerable degree of preferred orientation is easily detected. There are about 10^{12} atoms in the blocks here proposed to explain the colloid patterns. This figure is in good agreement with estimates of domain size made from Barkhausen noise, which range from 10^{10} to 10^{15} atoms⁸.

EFFECT OF TRANSVERSE FIELD ON FINE PATTERN

If a small field was applied parallel to a $\{100\}$ surface in addition to the usual normal field, simultaneous observation with the microscope revealed surprising changes taking place in the mazelike pattern. The lines of colloid would move locally by jumps equal to the width of one block. Lines meeting at corners were particularly sensitive to changes in transverse field. If the transverse field was turned on and off, the normal field remaining constant, each throw of the switch would produce a new maze having the same general appearance as previous mazes, yet differing in details. All of the many patterns to be seen, however, were consistent with the view that blocks retain their identity during the changes. The changes, apparently, are brought about by rotation of the direction of magnetization in the individual blocks to one of the other seven possible directions (of forms $\langle 100 \rangle$ and $\langle 110 \rangle$) lying in the surface. Upon increasing the transverse field to values producing approximate magnetic saturation, the fine pattern disappeared, leaving only a few broken streaks of colloid perpendicular to the transverse field.

A novel scheme was hit upon to study changes in the fine pattern under the conditions described above. A colloid pattern was deposited with normal field, the excess colloid was rinsed off with water and the surface quickly dried with compressed air. Such a procedure left the colloid pattern intact, and firmly attached to the surface. Then another colloid pattern was formed and the specimen subjected to a transverse field. The two patterns, one fixed and one changing with the transverse field, could be observed simultaneously. It was plainly evident that the blocks that could be located from the old pattern were responsible for the new patterns. That such is the case, even though the specimen in the meantime suffers complete magnetic saturation in arbitrary directions, will be obvious from a study of Fig. 9.

These patterns, taken on A_3 , show the combined new and old patterns with no field and with normal field in the original and reversed directions. Before the deposition of the new pattern the specimen was removed from the vertical magnet and arbitrarily moved around in a field sufficient to saturate it parallel to its surface. The fixed pattern may be identified in the no-field pattern.

Another experiment with transverse field demonstrated the relative importance of magnetic history as compared with the polishing history. The disk D was polished with the two directions of coarser polish coincident with the $\langle 100 \rangle$ directions most nearly in the face of the disk, followed by the usual nonpreferential polish with MgO paste. Photographs were made of the same region with normal field alone, following, respectively, several saturation reversals in the $[100]$, $[110]$, $[010]$ and $\bar{1}10]$

directions lying in the plane of the disk. The regions selected, Fig. 10, show the same scratch near the left (west) side of each photograph. This scratch was made by some contamination of coarser emery on the 0000 polishing paper.

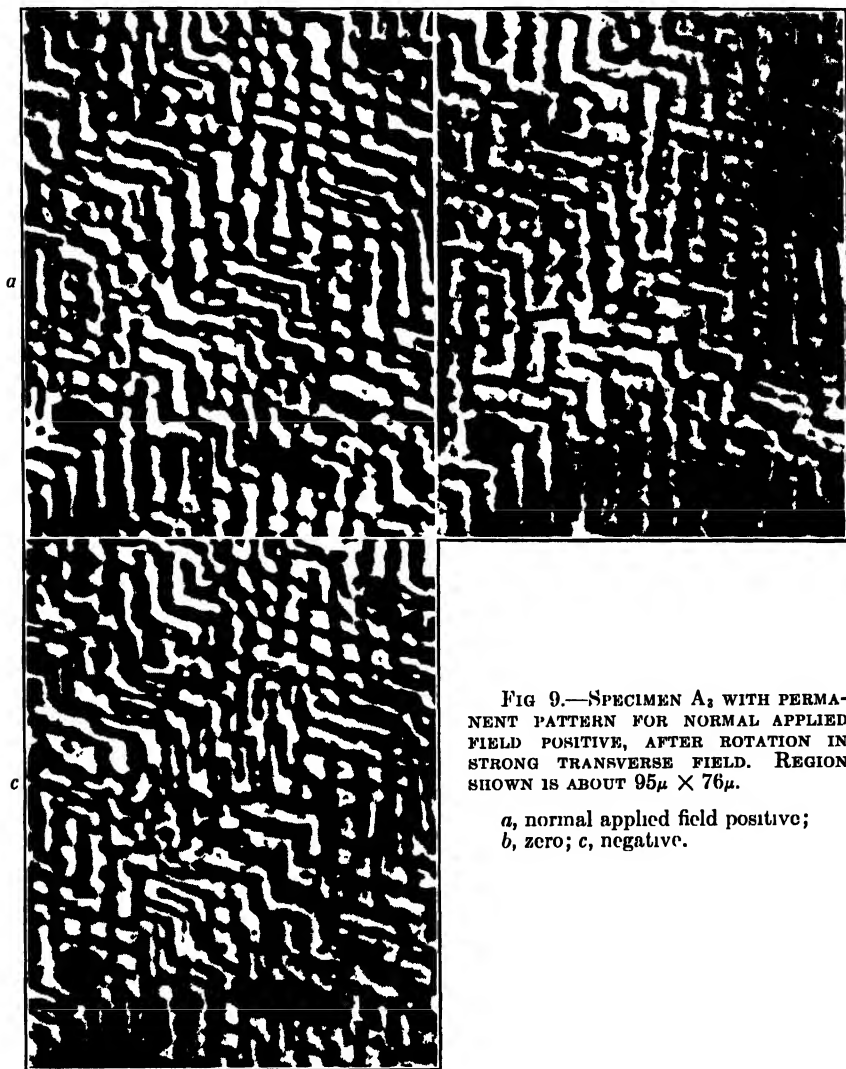


FIG 9.—SPECIMEN A, WITH PERMANENT PATTERN FOR NORMAL APPLIED FIELD POSITIVE, AFTER ROTATION IN STRONG TRANSVERSE FIELD. REGION SHOWN IS ABOUT $95\mu \times 76\mu$.

a, normal applied field positive;
b, zero; *c*, negative.

The part played by magnetic history is at once evident. Lines tend to form perpendicular to the previous direction of saturation. Therefore they appear as two sets of parallel lines or as two sets of steplike lines depending upon the direction of saturation, the latter corresponding to saturation along face diagonals of the blocks. In the region of the

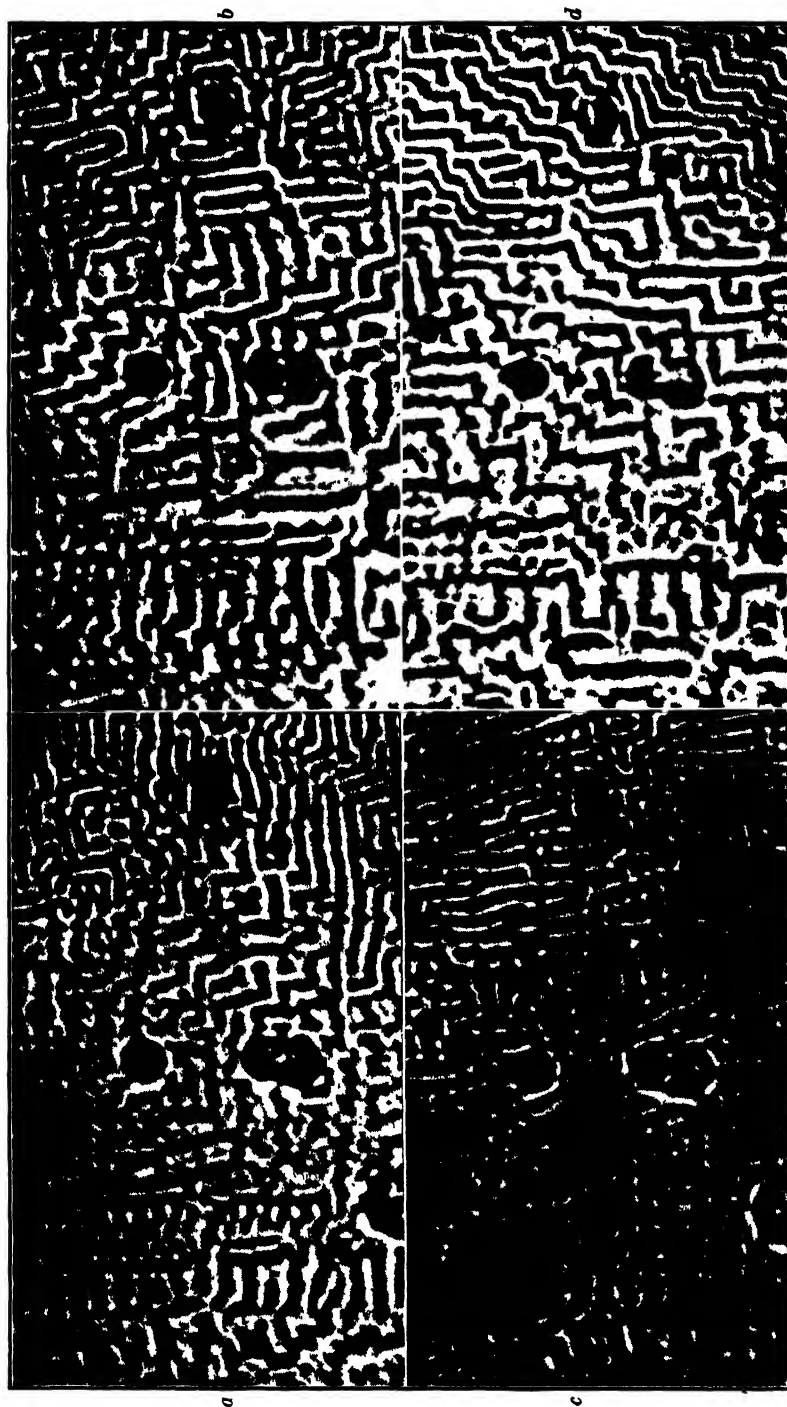


Fig. 10.—Directions designated map-wise. Specimen D.
a, last transverse saturation N-S; *b*, NE-SW; *c*, E-W; *d*, SE-NW.

scratch, however, the situation is not so simple. The lines have a greater spacing with a fine structure showing between them. Lines perpendicular to the scratch occur most frequently when there has been no component of the previous magnetic field along the scratch.

The experiments with a transverse field emphasize the stability of the block boundaries in the crystal lattice. The individual block has been found to keep its identity throughout any arbitrary magnetic treatment. This conclusion accords with the explanations proposed for the fine structure of lines and for the dot structure found in patterns with wider line spacings.

We hoped that more information could be obtained by heating a crystal above its Curie point. In particular, do the blocks retain their identity after losing and subsequently regaining their spontaneous magnetization? This question could not be answered with certainty, since heating the polished specimen A_3 in vacuum by an induction furnace even for as short a time as one minute at 850° C. resulted in random recrystallization of the polished surface and consequent disappearance of the magnetic structure pattern. Complete repolishing, however, removed all the new crystals and yielded the usual maze pattern having the same average spacing of lines as in the original state.

The important part that magnetic history plays as compared with polishing procedure has been shown. This new result substantiates the conclusion already reached that the existence of a thin polished layer suitably produced is merely incidental to the production of patterns and not an essential condition for block formation.

An explanation of the remarkable stability of the block boundaries is called for. What determines that the electron spins responsible for ferromagnetism (according to the Heisenberg-Weiss theory)⁹ should select only certain planes in the crystal for reversal? How does it happen that some stray field is present at the boundaries of the blocks even when they are arranged in sequences? Evidently the boundary regions are in some way peculiar. We suggest that foreign atoms segregated along these planes may be responsible for the stability of the magnetic block structure. Evidence for this sort of segregation has been found in non-ferromagnetic crystals.¹⁰ A possible mechanism for such a segregation may be found in the systematic imperfection of crystals that Zwicky¹¹ advocates, or in a lineage theory depending on conditions during crystal growth, such as Buerger¹² has advanced. Since demagnetization requires minimum stray field to be present in the crystal, the boundaries, if they become fixed below the Curie point temperature, would tend to assume the symmetrical arrangement (consistent with the crystal lattice) that would bring this about. If, as seems more probable, segregation occurs at higher temperatures, some nonmagnetic mechanism must be invoked.

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DISCUSSION

(Francis B. Foley presiding)

L. W. MCKEEHAN.—This picture is not in the paper.* It shows a different type of pattern obtained on a nickel crystal. The difference is quite striking. Instead of having a pattern of lines, it has a pattern of dots. The reason is not hard to see. In nickel, the direction in which small crystal units will naturally align themselves is a cube diagonal instead of a cube edge. It is quite impossible to arrange a system of cubical blocks magnetized along their diagonals so that they will produce uniform line boundaries.

C. S. BARRETT,† Pittsburgh Pa.—We have been studying the mechanism of slip in some of these same crystals furnished by Mr. Ruder, containing approximately 3.5 silicon. While the work is not yet completed it is far enough advanced to show definitely that the slip planes are not cube planes, which are the planes marked out by this method. The slip mechanism appears to be different at different temperatures, but in no case is there evidence of slip on cube planes. Of course, one would hardly expect a correlation between the planes that are important in magnetism and in mechanical deformation.

L. W. MCKEEHAN.—If the magnetically important planes are specially supported planes, one would expect they would be the last planes to slip.

W. E. RUDER,‡ Schenectady, N.Y.—This work of Elmore and McKeehan has considerably advanced our knowledge of these domains because of the careful way in

* A similar pattern has been published elsewhere. See *Phys. Rev.* (1934) [2] **46**, 529–531.

† Physicist, Metals Research Laboratory, Carnegie Institute of Technology.

‡ Metallurgical Engineer, General Electric Co.

which the work was done, by the use of colloids, and by the extreme regularity of the patterns presented. Of the various reasons given for the occurrence of these patterns, none seems to me to be entirely adequate. The authors' suggestion that there might be deposited impurities along the crystal planes is plausible, although it seems hard to believe that these deposits would be so regular. Of course, we do not know just what the atomic forces are and how they work, but the regularity of these patterns seems to me to be rather against that idea. I should like to see an experiment tried to check this.

We know, for example, that silicon iron, pure iron, or any other ferromagnetic materials subjected for a long time to a high temperature and extremely pure hydrogen can be freed of practically all of their impurities. Just how complete this purification would be, we do not know, but it seems that such an experiment might throw some light upon the proposed explanation given by Dr. McKeehan. I did not understand just what his explanation was for the increase in distance between lines of from 2 to 6μ by his preferential polish. This would seem to be just a matter of increased strain on the surface. No mention has been made of etching after this polishing, although it must have been tried. If so, what happens to the block pattern when the strained surface is removed by adequate, careful etching? I believe that the work now being done on these patterns is going to lead us a long way in the direction of a solution of the problem of the unit of ferromagnetism, and I congratulate the authors on the excellent piece of work that they have done.

L. W. McKEEHAN.—In regard to the effect of polishing, we have found which of the boundaries show most prominently after a directional polish. The result is that if you polish in a particular direction the boundaries perpendicular to that direction will show more prominently in the patterns then developed. It is the same set of boundaries in which the multiple arrangement of blocks will show up with preferential work that is still more severe. So far as we have observed, there is no change in the dimensions of the blocks. Working simply determines in which of the various directions they will be magnetized when they are left alone and whether they will reverse at every boundary as they apparently do in the least polished or most annealed state, or whether there will be chains of them agreeing in a direction giving the widest spacings in the pattern.

It is easy enough to see that strain can stabilize a particular direction, but it is not easy to see how the strains will affect the reversals along a direction. Perhaps, if the strain is sufficiently deep, so that the blocks are made less different from their boundaries than they were in the annealed state, the boundaries will have a smaller chance to show themselves.

F. B. FOLEY,* Philadelphia, Pa.—Do you have an explanation for the lines that appear, the heavier deposits?

L. W. McKEEHAN.—They are due to something that occurs deeper in the structure, and the best guess one can make at it is that a layer of blocks some distance below the surface is magnetized normal to the surface instead of parallel to it. This will result in an intensification of the normal field in one direction above the surface over that pile of blocks, as if one had a concealed dike of magnetic material under the surface. Of course, the surface itself apparently controls the magnetization so completely, that you do not see any surface blocks magnetized normally. But deeper in the material the surface is forgotten and there is nothing to prevent blocks from magnetizing in all three of the appropriate directions.

* Superintendent of Research, The Midvale Company.

L. W. McKEEHAN (written discussion).—One of the questions raised by Mr. Ruder was whether patterns can be observed on etched surfaces. At the time the paper was presented we had had no success in this attempt, as the surfaces became so rough that local elevations concentrated the colloid more than small changes in the magnetic field. More recently, however, Mr. Elmore has been able to obtain fine scale patterns on the smooth parts of etched surfaces. The experiments have not gone far enough to indicate whether the scale of these patterns is markedly different from that obtained on a polished face of the same crystal.

Initial Stages of the Magnetic and Austenite Transformations in a Carbon Steel

BY I. N. ZAVARINE, * ASSOCIATE MEMBER A.I.M.E.

(Chicago Meeting, October, 1935)

THE present paper is a continuation of the work on the relationship between the magnetic and the phase transformations in carbon steels during quenching. An account was given by the author in a previous paper[†] of an investigation of this relationship during a continuous quench. The experimental difficulties then encountered prevented a conclusive proof of the existence or absence of such a relationship. The conclusions of the previous paper were derived indirectly. The present paper deals with the same problem, but the method of attack is modified. The technique developed by Davenport and Bain² in their well-known study of austenite transformation at subcritical temperature was adopted in the present investigation. They have shown that the austenite to martensite transformation can be caused to proceed at a relatively slow rate by quenching steels into a hot metal bath. Slowing down of the rate of transformation, together with an observation by Lewis³ that a eutectoid steel can be preserved in the nonmagnetic state by such quenching, pointed out a possibility of a study of both transformations under more favorable conditions than previously described.

The preliminary steps were connected with the technique of the hot bath quench. To study this phase of the present work a modification of the apparatus previously described¹ was used. The modification consisted in the use of a hot quenching bath instead of brine, and in fixing the secondary and the primary coils of the apparatus in a stationary position in and around the bath. Tubular specimens, as in the previous investigation, were heated in a suitable furnace to a temperature in the austenitic range for the given steel and then were dropped into the quenching apparatus. The quenching bath was heated to a series of temperatures within the probable range at which the austenite to martensite transformation was expected to proceed at the slowest rate. Observations

Manuscript received at the office of the Institute June 12, 1935.

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† References are at the end of the paper.

were made on the change of magnetic flux with time for a given set of conditions, such as the nature of quenching bath, its temperature, and the temperature of the specimen before quenching.

The observations of the preliminary work can be summarized as follows:

Experience with two quenching media, lead-bismuth eutectic and

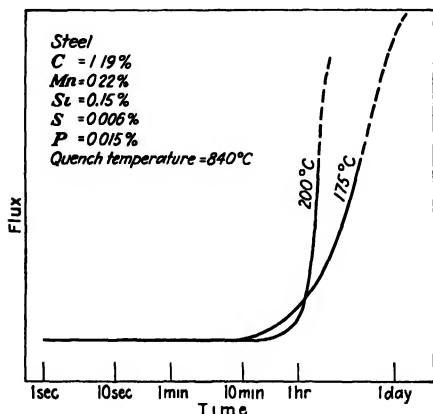


FIG. 1.—RATE OF MAGNETIC TRANSFORMATION AT 175° AND 200° C IN 1.19 PER CENT CARBON STEEL.

molten salt, has shown that the former was far less effective in retaining samples in nonmagnetic state. The bath that proved to be the most satisfactory from this point of view consisted of a commercial tempering salt with a layer of wet calcium chloride spread over its surface just before quenching. The function of wet calcium chloride was to promote the agitation of the bath at the time of quenching.

Quenching experiments with different carbon steels have shown that for the retention of austenite after quenching there exists an optimum temperature of the austenite before quenching and optimum quenching-bath temperature. Under these conditions the magnetic transformation is delayed for a considerable time. The transformation proceeds at an accelerated rate with deviation from the optimum conditions. An example of observations obtained for the samples of 1.19 per cent carbon steel is given in Fig. 1. The curves show the rate of transformation in this steel after quenching into a salt bath held at 175° and 200° C.

The magnetic transformation in low-carbon steels starts immediately on quenching and proceeds rapidly. Appreciable delay of the beginning of the transformation is observed with a 0.60 per cent carbon steel. The delay is further increased with increasing carbon content of steels. The previous history of the steel was found to affect the form of the transformation curve. Preliminary quenching, for instance, was found to delay the beginning of the transformation.

The experimental work proved that under controlled conditions medium and high-carbon steels could be retained in a nonmagnetic state for an appreciable time. Once started, the magnetic transformation proceeds to completion at a rate depending on the conditions. There is no means of interrupting this process at an intermediate stage.

The problem of the selection of a parameter defining the phase transformation presented itself at this stage of the investigation. The austen-

ite transformation is accompanied by a number of physical phenomena, such as thermal, volumetric effects, change in electrical conductivity, change in space lattice, etc. These manifestations of the transformation are unquestionably related, but the basic phenomenon is the transformation of the space lattice. Austenite is a solid solution of carbon in the face-centered cubic lattice⁴. The structure of quenched carbon steel may consist of an aggregate of solid solutions of carbon in the body-centered cubic, body-centered tetragonal and the face-centered cubic lattices. The tetragonal solid solution is considered by many investigators as an intermediate step in the transformation from the face-centered to the body-centered cubic solution. It was shown by Hägg⁵ and others⁶ that the tetragonal solid solution is stable at temperatures not exceeding 150° C. and changes to the body-centered cubic type at higher temperatures. Because the austenite was caused to transform in the present investigation at a temperature above 150° C., the tetragonal lattice can be left out of the consideration. The following work is an attempt to correlate the magnetic transformation with the lattice transformation of austenite quenched into a hot bath.

The apparatus used in the preliminary work was not suitable for the X-ray investigation. A schematic arrangement of the apparatus shown in Fig. 2 was found workable. A wire, 0.015-in. diameter, was heated to the quenching temperature by passing it through a vertical electric furnace. On leaving the furnace the wire was quenched into a bath of hot molten salt. The direction of the wire motion was then changed by suitable pulleys immersed in the bath and the wire was continuously drawn through an X-ray camera. On leaving the camera, the wire passed through a transformer which, together with suitable amplifier and galvanometer, served to indicate the magnetic state of the wire at the time of its exit from the camera. The wire was set in motion by a drum 10 in. in diameter actuated by an electric motor through a suitable speed-reduction train. The object of this arrangement was to heat the wire to a temperature in the austenitic range, to quench it into a hot bath to

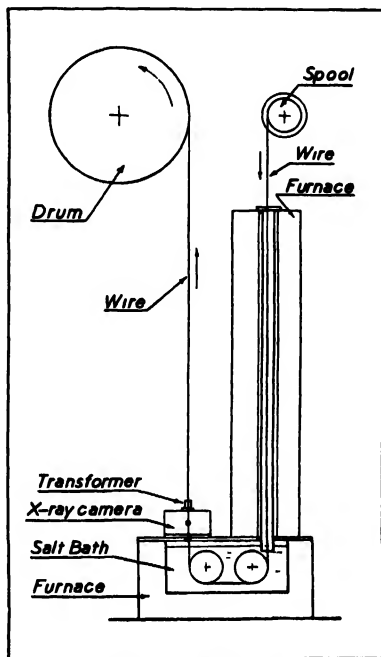


FIG. 2.—DIAGRAMMATIC SKETCH OF APPARATUS.

preserve the austenite at a low temperature, and then to draw the wire into the X-ray camera at a speed sufficient to bring a section of the wire into the X-ray beam before the beginning of the magnetic transformation. Experience has shown that this object can be accomplished under certain conditions indicated later in Table 1.

The chemical composition of the original wire was: carbon, 0.87 per cent; manganese, 0.42; silicon, 0.15; sulfur, 0.024; phosphorus, 0.011; chromium, 0.17; nickel, 0.16.

The wire passed through the apparatus at a velocity of 110 in. per minute, which corresponds to 13 sec. heating period in the furnace, 6 sec. in the quenching bath and slightly less than one second for any given point of wire to reach the X-ray beam after leaving the surface of the quenching bath.

The temperature of the quenching bath most advantageous from the point of view of retaining the wire in the nonmagnetic state for the longest time was between 190° and 200° C. The experimental runs were started with the bath at 190° C. and finished at 210° C. The increase in the bath temperature was due to conduction of heat from the high-temperature furnace.

The X-ray camera of the Debye-Scherrer type was used with chromium radiation. A 45-min. exposure was found satisfactory. This length of exposure required about 0.5 lb. of wire for each run.

The problem of prevention of decarburization of the wire was solved by continuously introducing the vapor of a commercial liquid carburizer into the high-temperature furnace. The third column of Table 1 shows the carbon content of the quenched wire. It can be seen from the table that a strongly carburizing atmosphere was created in the heating furnace, as shown by the carbon pick-up at higher temperatures. The fact that the wire could be retained in the nonmagnetic state also proves that decarburization was not present. Preliminary experiments have shown that steels with a low carbon content transform almost instantaneously on quenching into a hot bath. Slight carburization of the wire should not invalidate the results presented because the product of the austenite transformation is grossly martensite for eutectoid and hypereutectoid steels.

Experience has shown that the different stages of the austenite transformation can be obtained by a simple expedient of controlling the temperature of austenite before quenching. The second column of Table 1 shows the temperature of the heating furnace and not of the wire. The temperature of the moving wire was not measured. The temperature of the wire unquestionably lagged behind the temperature of the furnace, as shown by the observation that the wire quenched from a furnace temperature of 845° C. developed occasional soft spots. These later observations are not included in the table.

TABLE 1.—*Simultaneous Observation of Magnetic Transformation and Lattice Structure of Wire*

Run No.	Furnace Temperature, Deg. C.	Carbon Content of Wire after Quenching, Per Cent	Magnetic State of Wire	Lattice
1	1000	0 99	Nonmagnetic	Face-centered cubic exclusively
2	930	0 89	Nonmagnetic	Face-centered cubic and body-centered cubic
3	875	0 87	Slightly magnetic	Body-centered cubic, predominantly, and face-centered cubic

The fourth column of Table 1 gives the results of the magnetic observations, the last column shows the results of the lattice measurement. The descriptive terms of the type of lattice were considered sufficient for the present investigation. The table shows that a small wire of eutectoid (or hypereutectoid) steel when heated sufficiently and quenched into a salt bath at about 200° C. will be preserved in a truly austenitic state. Seven seconds after quenching it will have a face-centered lattice structure and will be nonmagnetic. When the wire is heated to a lower temperature and quenched under similar conditions, the austenite becomes less stable and 7 sec. after the beginning of quenching it is half transformed to a body-centered cubic solid solution. However, the transformation is not accompanied by a recovery of ferromagnetism. When a still lower quenching temperature is used, the austenite transforms almost completely to a body-centered cubic solid solution before the appearance of the ferromagnetism.

DISCUSSION OF RESULTS

The austenite to martensite transformation involves a transformation from a face-centered to a body-centered cubic solid solution of carbon in iron. The transformation is accompanied by a series of physical phenomena, one of which is a change from the paramagnetic to the ferromagnetic state. It is shown in the present paper that the initial stages of lattice transformation in a high-carbon steel do not coincide with the magnetic transformation, the lattice transformation preceding the magnetic transformation. Howard Smith⁷, investigating a manganese steel, also found that the lattice transformation precedes the magnetic transformation. Limited experimental evidence precludes the drawing of general conclusions, but the available information points to a lack of relationship between the magnetic and the phase transformations of austenite in carbon steels during the initial stages of quenching.

SUMMARY

1. Evidence is presented that the initial stages of magnetic transformation in medium and high-carbon steels quenched into a hot bath are delayed for a measurable time, depending upon the quenching conditions and the carbon content of the steel.

2. It is shown that the lattice transformation of a eutectoid steel quenched into a hot bath does not coincide with the magnetic transformation, the lattice transformation preceding the magnetic transformation.

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X-ray Study of Iron-nickel Alloys

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(New York Meeting, February, 1936)

THE unusual physical, electrical and magnetic properties of the iron-nickel alloys has given rise to a voluminous literature. This work will be reviewed critically in "The Alloys of Iron and Nickel," a monograph of the Alloys of Iron Research Series, soon to be published. In what follows we shall therefore confine ourselves to those of the earlier investigations that involved the use of X-ray crystal-structure methods.

The earliest X-ray work on the iron-nickel system was by Miss Andrews¹. Using the powder method of X-ray analysis purely as a means of identifying the phases present, she located a region between 20 and 30 weight per cent nickel in which body-centered and face-centered phases coexisted. No lattice constants nor details of heat-treatment were reported. Bain² also reported some qualitative observations.

McKeehan³ made a systematic investigation over the whole of the system, giving many of his alloys four and some five different heat-treatments. In alloys furnace-cooled from 900° to 950° C. he found two coexisting phases between 0.15 and 30 per cent nickel. The precision of the lattice-constant measurements was low in comparison with what can be obtained today. Even for alloys of the same heat-treatment, differences in the constants were often between two and ten parts per thousand. In regions where no change of lattice constant with heat-treatment should occur, differences of the same order of magnitude were found. Since the maximum change in the lattice constant of nickel with change of composition is only about 2 per cent of the constant for pure nickel, these variations in the constants for a given alloy cause the points to "scatter" badly about any curve that may be drawn to represent them and it is difficult to interpret such results. In spite of this, McKeehan shows that the lattice constant of nickel increased as the iron content increased. His results for the alpha-iron phase are less conclusive.

Osawa⁴ also investigated the entire system. For alloys slowly cooled from 1150° C. and then filed into samples for X-ray analysis, he found

Manuscript received at the office of the Institute Nov. 30, 1935.

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the first indication of the two-phase region in an alloy containing 27.07 per cent nickel and the last traces at 35.27 per cent. After immersion in liquid air, the two-phase range was found between 27.66 and 35.27 per cent nickel. The accuracy of Osawa's lattice-constant measurements was apparently higher than those of McKeehan. He found the lattice of nickel to expand on the addition of iron and also an expansion of the alpha-iron lattice upon the addition of nickel.

Jung⁵ determined the lattice constants of 10 iron-nickel alloys. His results did not check the extent of the phase regions found by Miss Andrews but the lattice-constant values agreed with McKeehan's within the limits of accuracy then attainable.

Roberts and Davey⁶ investigated the A_2 transformation point of pure iron and a number of iron-nickel alloys up to 13 per cent nickel by special X-ray methods. Using a camera in which the specimen could be heated to any desired temperature, they used the resulting films to detect the presence or absence of the body-centered and face-centered structures. Working in small temperature intervals they found all body-centered or all face-centered structures at temperatures only 5° C. apart. Only in one case were they able to find both structures coexisting, but a repetition at the same temperature gave only one phase. All points for the alloys were determined on heating from room temperature to that desired. If the alloy were first heated above the temperature of the X-ray exposure it was found that the face-centered phase persisted over a temperature range that depended upon the nickel content of the alloy. They conclude, "In other words, the A_2 point is not one at which the change is reversible." It is difficult to decide from this article whether the authors believe that the gamma-alpha transformation in iron-nickel alloys is precisely the same, except for temperature, as in pure iron, or that the two-phase region for any composition over the range covered corresponds to a temperature interval of 5° C. or less. The former is certainly at variance with the phase rule, while the latter differs from the results of all other investigations, including those to be reported below. The measurements of the lattice constants of their alloys from films taken in the well-known General Electric apparatus differ widely from those found in the present investigation.

Phragmén⁷ determined a number of lattice constants of low-carbon ($C < 0.05$ per cent) nickel steels in the course of his work on the thermal expansion. His alloys were largely confined to the Invar region. His results agree well with those reported below and will be referred to later.

Dehlinger⁸, in an article on the kinetics of "the irreversible transformation in the system iron-nickel," includes photograms of a 29 per cent nickel alloy that show the two phases at -80° C. but only the alpha phase at -180° C.

Quite aside from the uncertainty in the phase diagram of the iron-nickel system, the discrepancies between the quantitative values of the lattice constants given in the earlier work and the limited range of compositions used in the more precise investigations of Phragmén made it necessary for us to reinvestigate the whole system. Our primary object was to secure the curves of lattice constant versus composition for the alpha and gamma-phase structures, because these data are necessary for another investigation that is in progress. Incidental to this work, certain observations were made that are of interest in connection with the phase diagram. These observations are included in this report, in spite of their obvious incompleteness, for the reason that further work on this system must be postponed indefinitely; they may be of interest in connection with data from other sources.

MATERIALS AND METHODS

Carbonyl iron was used for making all of the alloys. Analysis by the Union Carbide and Carbon Research Laboratories, Inc. gave: C, 0.007 per cent; Si, 0.004; S, 0.004 and a trace of Mn. The nickel was of electrolytic origin and contained 0.013 per cent Fe, 0.11 per cent Co and traces of Si and S. Spectroscopic tests revealed no appreciable amounts of other metallic impurities.

Weighed quantities of these metals were placed in alundum crucibles and melted in vacuo by means of a high-frequency induction coil. The ingots weighing 30 to 40 grams were then annealed at approximately 1000° C. for one week in a hydrogen atmosphere and cooled in the furnace. Powders were then prepared by grinding with a small alundum wheel. These powders were sealed into evacuated glass or quartz tubes for the final annealing, the time and temperature of which is recorded in the tables. The coarser particles were removed with a 100-mesh sieve. The long-time, low-temperature anneals were carried out in small horizontal furnaces, and the samples were quenched in water. The higher-temperature and shorter anneals were done in vertical quenching furnaces, which have already been described⁹. The sample tube is crushed as it strikes the quenching liquid (water) and the quenching time is estimated to be of the order of a few hundredths of a second.

Samples for analysis were cut from the annealed ingots. Nickel was determined on the low-nickel alloys by the dimethylglyoxime method. In the other alloys, iron was determined by reduction to ferrous iron in a silver reductor followed by a titration with ceric sulfate solution using ferrous phenanthroline as an indicator¹⁰.

The X-ray cameras used for the lattice-parameter measurements were of the type recently described by the authors¹¹. The technique of

film measurement and calculation given in that article has been followed in most cases. Some of the films could not be measured by the photometric method because of the spottiness of the lines arising from too large grain size. This was apt to occur on films of alloys annealed for too long a time at high temperatures. The precision is generally, but not always,

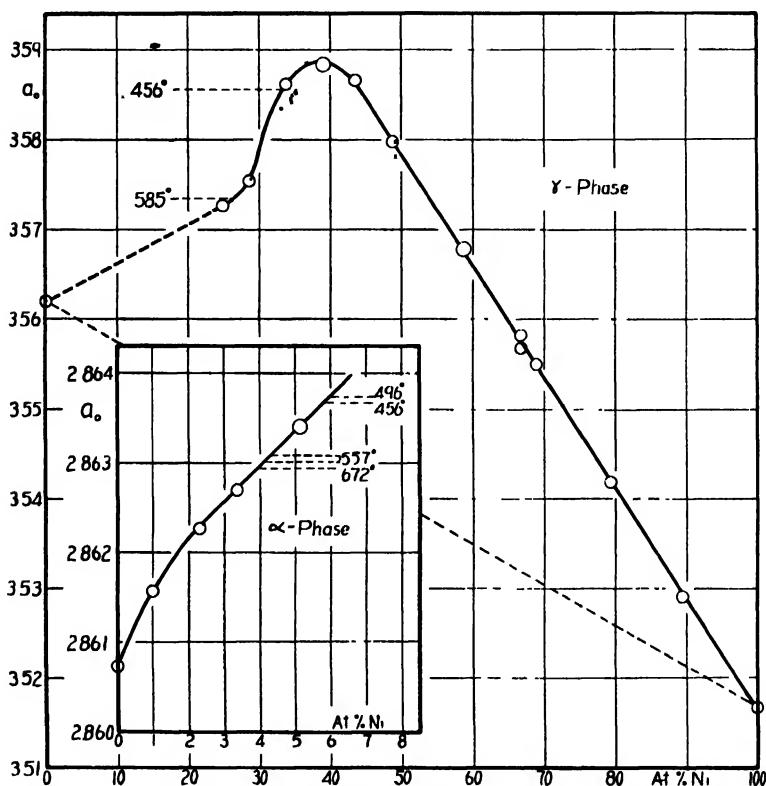


FIG. 1.—LATTICE CONSTANT VERSUS COMPOSITION.
 ○ Jette and Foote × Phragmén.

better on films that had been photometered than on those measured with a glass scale but the difference was not important. The limit of accuracy stated for each film is not the usual probable error but a somewhat larger quantity called the fiducial limit. The method of obtaining this quantity and the reasons for its use have been given by the authors¹¹. In the results below, it generally does not exceed one or two parts per ten thousand.

In order to secure a sufficiently large number of properly distributed diffraction lines in these cameras, radiation from alloy targets was used. The best set of wave lengths for alpha-phase alloys was obtained from an X-ray target of iron and cobalt; for gamma-phase alloys, of iron and

manganese. For the alpha-phase alloys reflections of Fe-K α radiation from 220 and of Co-K α from 310 planes were secured. For the gamma-phase alloys, reflections of both Fe-K α and Mn-K α radiations were obtained from the 311 planes, and of Fe-K α from the 222 planes. The alpha doublets were resolved in all cases. A correction for refraction was applied¹¹. When it was desired to verify the presence or absence of one of the phases, the inner and middle range focusing cameras designed by Phragmén were used.

LATTICE CONSTANTS OF THE GAMMA-PHASE ALLOYS

The results of the lattice-constant measurements in the gamma-phase alloys are given in Table 1 and Fig. 1. The plot shows three regions. From 100 to 43 atom. per cent nickel, the lattice constant is a linear function of the composition. The equation representing these results is:

$$a_0 = 3.64033 - 0.0012379 (\text{atomic per cent Ni}) \quad [1]$$

TABLE 1.—*Lattice Constants of Gamma-phase Alloys*

Film	Sample	Powder Anneal		Atomic Per Cent Nickel	a_0 (25°)
		Time, Hr.	Temp., Deg. C		
	Ni			100 00	3 5168, \pm 0.0000 ₈
VII-177	11x	2	578	89 56	3.5292 ₇ , \pm 0.0004 ₈
VIII-12	11b	2	950	89 56	92 ₇ , \pm 0.0000 ₈
X-21	11N	195	597	89.40	87 ₈ , \pm 0 0002 ₈
X-21	11N	195	597	89.40	89 ₈ , \pm 0.0000 ₈
VIII-40	10x	3	578	79 43	3 5417 ₈ , \pm 0.0005 ₄
VIII-14	10b	3	973	79.43	18 ₈ , \pm 0.0003 ₂
VIII-13	9xb	3	548	69.05	3 5549 ₄ , \pm 0.0003 ₈
X-45	15	1560	447	66.79	66 ₈ , \pm 0 0004 ₈
X-4	15	642	582	66 79	81 ₈ , \pm 0 0002 ₀
VIII-41	8x	3	548	58 77	3.5682 ₂ , \pm 0.0002 ₈
VIII-39	8x	3	548	58 77	74 ₈ , \pm 0.0003 ₁
VIII-36	7x	3	548	48.72	3 5798 ₄ , \pm 0.0004 ₂
VIII-48	7x	2	950	48 72	97 ₂ , \pm 0.0003 ₈
X-1	12	475	581	43.57	3 5865 ₈ , \pm 0 0003 ₇
VIII-59	6	13	546	39.16	84 ₂ , \pm 0 0006 ₇
VIII-37	6x	3	548	39.16	81 ₇ , \pm 0 0003 ₄
VII-270	6	23	558	39 16	82 ₂ , \pm 0.0006 ₁
VIII-46	6	2	950	39 16	87 ₈ , \pm 0 0004 ₈
X-2	13	475	581	33 80	62 ₄ , \pm 0 0005 ₈
VIII-58	5	13	546	28.59	3.5757 ₁ , \pm 0.0001 ₈
VIII-38	5	3	547	28 59	53 ₇ , \pm 0.0004 ₂
X-39	5	20	689	28 59	54 ₈ , \pm 0.0002 ₁
X-40	14	20	689	24 81	27 ₄ , \pm 0.0003 ₈
(Öhman)	γ -Fe			0.00	3.562

Between 43 and approximately 20 atomic per cent nickel the curve is roughly S-shaped. This behavior was entirely unexpected and just what it may mean is not clearly known. It is in this range of compositions that most, if not all, of the physical, electrical and magnetic properties show peculiar variations with both composition and temperature. In this connection it should be emphasized that while the alloys were annealed at high temperatures, all the lattice-constant measurements were made within a few degrees of 25° C. This portion of the plot shows a rather flat maximum at 39 atom. per cent nickel. The lattice parameters in this region are independent of the quenching temperatures. Phragmén's work on Invar included a number of lattice-

TABLE 2.—*Lattice Constants of Alpha-phase Alloys*

Film	Sample	Powder Anneal		Atomic Per Cent Nickel	a_s (25°)
		Time, Hr	Temp., Deg C.		
	Fe			0 00	2 8607 ₄ ± 0.0001 ₀
X-43	16	190	553	0.99	15 ₇ ± 0.0000 ₆
VIII-68	1	58	555	2 32	22 ₇ ± 0.0001 ₄
X-24	17	190	553	3.37	26 ₉ ± 0.0000 ₃
X-14	2	3150	456	5.16	33 ₉ ± 0 0001 ₆
VII-282	2x	3	547	5 16	33 ₇ ± 0 0003 ₈
VIII-5	2xb	3	624	5 16	34 ₆ ± 0.0002 ₄
X-41	2	38	628	5 16	34 ₀ ± 0 0006 ₈

constant measurements in this region. His results, corrected slightly for expansion, since his determinations were reported for 10° C., are included in Fig. 1. These values in no case differ by more than 0.003Å. from the curve, and since they are all in the region where the effects of otherwise negligible amounts of foreign elements in either set of alloys is likely to be greatest, this agreement is excellent. He placed the maximum at about 37 atom. per cent nickel.

Below 25 atom. per cent nickel, the form of the curve of lattice constant versus composition cannot be directly determined. Öhman¹² extrapolated the lattice constants of iron-manganese alloys to pure iron and thus found for the lattice constant of gamma iron the value 3.562Å. This has been confirmed by Hägg¹³ from the austenitic iron-carbon alloys by a similar extrapolation. Using this value, unless the lattice constants vary in an unusual way, the curve between the last point determined (24.8 atom. per cent Ni) and pure iron will be practically a straight line between 0 and approximately 20 per cent nickel. The tentative character of the representation of this region in Fig. 1 must be emphasized first because direct determinations are impossible, and second, in this

same range of compositions the iron-chromium alloys show an abnormal variation (see Preston¹⁷).

Keeping in mind the reservations regarding the low-nickel alloys, we have in this system positive deviations from the additivity rule throughout the entire range of composition. The dotted line in Fig. 1

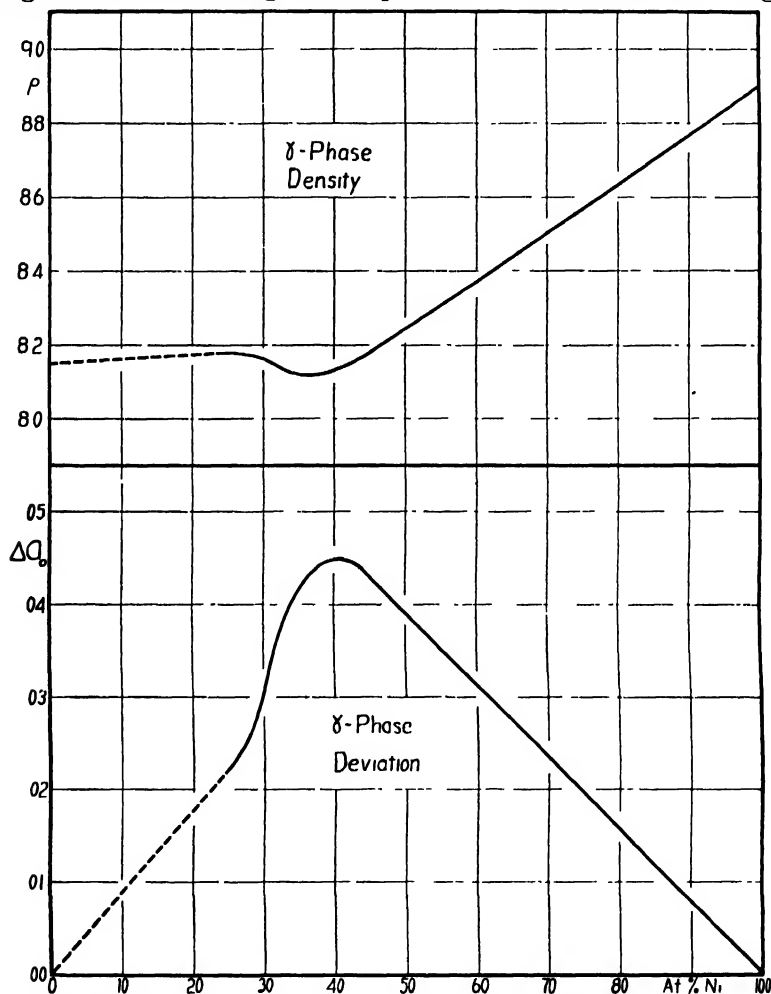


FIG. 2.—DENSITY VERSUS COMPOSITION. DEVIATION FROM ADDITIVITY RULE VERSUS COMPOSITION.

represents the additivity rule. The positive deviation between 43 and 100 atom. per cent nickel is greater than has been observed so far in any other system where a complete series of solid solutions is found uncomplicated by changes in coordination number¹⁵. A good idea of the extent of this deviation may be secured by calculating the value of a_0 for pure

gamma iron from equation 1, which gives 3.640\AA . instead of Öhman's value of 3.562. The difference is 2.17 per cent of the average lattice constant.

The deviations of the actual lattice-constant curve from the additivity rule is strikingly shown by the deviation curve in Fig. 2. Because of the flatness of the maximum on the lattice-constant curve and to the "tilt" of the curves¹⁷, the maximum shifts slightly to about 41 atom. per cent. It is noteworthy that between approximately 40 and 25 atom. per cent nickel the positive deviation drops to about one-half its maximum value. The positive deviations have been associated¹⁵ with repulsive forces between atoms. That such forces should change so rapidly between two atomic species, which are in many respects so similar that positive deviations would scarcely be expected at all, indicates far-reaching changes in the outer electron levels of the atoms. Most if not all the changes are probably associated with the 8 (Fe) and 10 (Ni) electrons lying beyond the argon "shell." The data in Table 1 and Figs. 1 and 2 when combined with data on other properties such as specific heats, expansion coefficients and magnetic properties should be useful in interpreting the various phenomena on a sound theoretical basis. It should be emphasized, however, that before any successful theory can be developed, the data used, particularly magnetic data, must be free from the effects due to the gross structure of the alloys such as grain size, intergranular material, mechanical strains, etc. The X-ray data reported in Table 1 are largely free from such influences.

LATTICE CONSTANTS OF THE ALPHA-PHASE ALLOYS

The lattice constants of the alpha-phase alloys are summarized in Table 2 and Fig. 1 (inset). Three facts are to be noted: (1) The plot shows that the variation of lattice constant with composition is not linear. (2) Since the nickel atom is smaller than the iron atom, the lattice constant of iron should decrease with the addition of nickel and an increase is observed. This is a striking positive deviation from the additivity rule. If the coordination factor¹⁵ is taken into account the amount of the positive deviation is even greater. (3) At temperatures of 450°C . and above, no alloy containing more than 5.2 atom. per cent nickel was solely in alpha-iron form.

THE TWO-PHASE ALLOYS

In this portion of the work we are on very much less certain ground. Every investigator on this system has been greatly troubled by two factors: (1) the impossibility of retaining the gamma phase by quenching

when the nickel content is low and (2) the sluggishness of the transformation at somewhat higher nickel contents, and particularly at low

TABLE 3.—*Lattice Constants of and Tentative Values for the Phase Limits*
ALPHA PHASE

Film	Sample	Powder Anneal		Atomic Per Cent Nickel in Alloy	a_s (25°)	α -phase Limit (Atomic Per Cent Nickel)
		Time, Hr	Temp., Deg. C.			
X-29	2	17	672	5.16	$2.8629_4 \pm 0.0042_7$	3.94
VII-272	3	24	557	9.60	$30_1 \pm 0.0013_1$	4.15
VIII-66	3	24	557	9.60	$30_8 \pm 0.0019_9$	4.30
X-32	3	734	496	9.60	$37_1 \pm 0.0005_4$	6.07
X-15	3	3150	456	9.60	$36_7 \pm 0.0004_4$	5.91

GAMMA PHASE

						γ -phase Limit
X-3	14	457	585	24 81	$3.5735_1 \pm 0.0001_7$	26.20
X-19	4	3150	456	19 31	$3.5856_6 \pm 0.0005_9$	33.36
X-20	5	3150	456	28 59	$55_9 \pm 0.0007_8$	33.36

temperatures. These factors have led to the "double diagrams" (for example, references 16 and 18) in which the two-phase region limits are entirely different, depending upon whether determined from alloys being heated or being cooled. They have led some investigators to the use of the term "irreversible transformation" between these two phases^{8,18}.

From the description of the method of preparing our alloy powders for X-ray examination, it will be evident that our results must be considered as obtained from severely cold-worked material raised from room temperature to that recorded in Table 3. This, of course, does not imply that the alloys were in an equilibrium state at room temperature. It is probable, however, due to the comparatively slow cooling of the ingots and the cold work produced in the preparation of the powders, that the actual compositions of the phase or phases corresponded in most cases to a range of temperatures below the temperature at which the final heat-treatment of the powder was performed.

Owing to the peculiarities of the low-nickel alloys, the X-ray technique does not yield the same clear-cut results that have been obtained in many other systems. Experience has shown that when the alloys contain 25 or more atom. per cent of nickel the gamma phase can be retained unchanged by quenching to room temperature. Thus if the gamma phase, which is in equilibrium with the alpha phase, contains at least 25 per cent nickel, the whole alloy can be quenched to room temper-

ature and the corresponding lattice constant has some significance for the determination of "solubility limits," whatever this term may finally mean in the iron-nickel system. The results in Table 3 show that this condition was reached only at low temperatures. For alloys annealed at a higher temperature, where the gamma phase has a lower nickel content, the gamma-phase lines, if they appear at all on the photograms, are so diffuse as to be unmeasurable.

The alpha boundary of the two-phase region at lower nickel contents can be determined only by choosing the experimental conditions in a

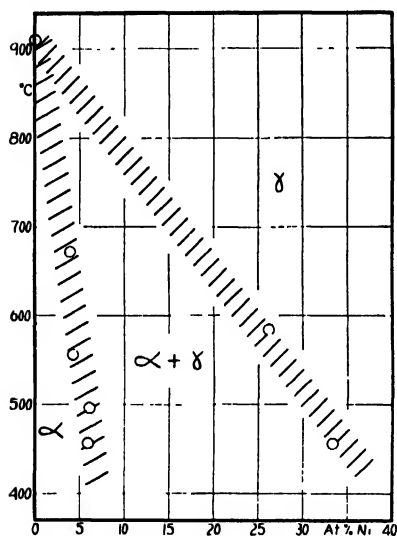


FIG. 3.—TENTATIVE EQUILIBRIUM DIAGRAM.

particular way and even then the results are none too satisfactory. The method is to find, for an alloy of given gross composition, a temperature at which the alloy is in the two-phase region but nearly all alpha phase. When an alloy is quenched from such a condition, the gamma phase, of course, decomposes, producing more alpha. If the amount of gamma phase was small, the sharpness of the alpha phase diffraction lines is not decreased too much and their positions are changed very little. It is evident that such a method involves a large number of experiments, and in any case the lattice-constant measurements must be interpreted with great care. The results of our application of this method are shown in Table 3 and Fig. 3. Highly tentative limits for the two-phase region are indicated in the diagram. The point at 585° C. near the gamma limit is based on the highly questionable assumption that two-phase equilibrium had been attained; no alpha-phase lines were observed, which would not be unexpected, since this alloy would probably lie very close to the gamma limit of the phase region.

A complete investigation of this whole region must await the construction of a high-temperature camera capable of high precision. Considerable accuracy is necessary for the determination of the alpha-phase limit because the alpha-phase range is not wide and the change of the lattice constant is small. The length of time a specimen would have to be held at the desired temperature while in the camera before taking the photogram would need to be determined largely by experiment. Such heating times might easily extend to 1000 hr. or more at temperatures below 500° C. It will also be necessary to investigate alloys that

have been brought to equilibrium in the camera at temperatures higher than the final temperature, and other alloys that were in equilibrium at temperatures lower than the final. Our experience thus far indicates very clearly that trustworthy information can be obtained only through a long series of carefully performed experiments.

In concluding this section on the two-phase alloys, we shall merely call attention to the fact that the alpha-phase boundary in Fig. 3 is not far from that found by other methods *on cooling* while the gamma boundary is near that similarly found *on heating*, but the latter curve is not drawn with the sharp outward bend indicated in reference 16. The points secured in the present investigation at 456° C. seem to be the most certain in this region and were secured by annealing at this temperature for 3150 hr. These results may be of some significance but the reader's attention is again called to the incompleteness of the investigation on which they are based.

EXISTENCE OF COMPOUNDS OF IRON AND NICKEL

The sharpness of the minima and maxima that are observed in a number of the physical, electrical and magnetic properties when studied as functions of composition have given rise from time to time to the assumption that compounds between iron and nickel exist. The previous X-ray work never revealed such compounds, although it must be admitted that the experimental work had not been designed particularly to demonstrate their existence. In an attempt to settle this matter, alloys spread over the whole composition range were annealed and quenched from two different temperature levels 950° and 550° C. and a few from about 450° C. None of these alloys showed signs of compound formation on the X-ray photograms. A number of experiments were also performed around 350° C. These alloys in ingot form were severely cold-worked several times with annealing periods of two weeks at 350° C. intervening. They were then made into powder form and again annealed for three weeks at this temperature. The lines on the film were too diffuse for lattice-constant determinations, but no lines other than those of alpha or gamma phases were present. This temperature seems to be too low to remove the mechanical strains in the lattice in the time allowed.

As far as X-ray evidence is concerned, no compounds exist in this system. The large positive deviation from the additivity rule in both the gamma-phase and alpha-phase alloys is in itself a strong indication that compound formation is absent.

The formation of superstructures, i.e., ordered arrangements of the nickel atoms in the iron lattice or vice versa, such as have been observed in a number of other systems, remains as a possible explanation of the peculiar variation of properties with composition. Ordinarily it is impossible to detect superstructures when the atomic species concerned

have atomic numbers that differ by less than 10. In the iron-nickel system, however, we may take advantage of the fact that the wave length of $K\alpha$ radiation from a nickel target falls inside a prominent X-ray absorption band for iron but just outside the corresponding band for nickel. Thus if the nickel atoms were in an ordered arrangement in the gamma-iron lattice, or vice versa, new reflections from planes containing only nickel atoms should be observed or, at least, the relative intensities of the reflection lines should change considerably. Experiments of this sort of alloys 5, 15 and 10 containing respectively 28.6, 66.8 and 79.4 atom. per cent nickel yielded no new diffraction lines. Visual examination of the films revealed no marked change in relative intensities among the diffraction lines from the different planes nor from $K\alpha$ and $K\beta$ lines from the same plane. Alloy 15, which has almost exactly the composition of Ni_2Fe , had been annealed for 1560 hr. at 447° C. to allow ample time for whatever atomic rearrangements were necessary. In spite of this long period, the photogram lines were still somewhat blurred, indicating that complete equilibrium had not been attained. The slightly lower value for its lattice constant is therefore of no significance with respect to superstructure formation.

DENSITIES

Densities calculated from accurate measurements of lattice constants† and the compositions are virtually independent of many of the factors that affect ordinary density determinations. This is true because the size of a fundamental quantity, the size of the unit lattice or cell, is measured. For this reason, such calculated densities are important in theoretical work. Density values for both the alpha and gamma-phase structures are given in Table 4. Attention is again called to the fact that the gamma-phase lattice constants were not determined in the range between 0 and 24 atom. per cent nickel. The density values in this region are starred. The curve (Fig. 2) shows a minimum at approximately 37 and a maximum at about 25 atom. per cent nickel.

ACKNOWLEDGMENTS

The work on this alloy system was begun by Mr. and Mrs. Allan L. Tarr. We take this opportunity to express our gratitude for their assistance in making and heat-treating a large portion of the alloys.

We also acknowledge our indebtedness to Mr. Willard L. Bruner for making the chemical analyses and to a number of students furnished

† With deviations from the additive rule of the sort found here there is no probability that lattice points are unoccupied. Calculations using published density data (Int. Crit. Tables, 2, 481), which are none too consistent, indicate that these alloys are of the simple substitution type.

TABLE 4.—*Densities*
GAMMA PHASE

Atomic Per Cent Nickel	ρ	Atomic Per Cent Nickel	ρ
100	8.902	45	8.180
95	8.833	40	8.134
90	8.765	35	8.122
85	8.698	30	8.165
80	8.632	25	8.179
75	8.566	20	8.173*
70	8.500	15	8.167*
65	8.435	10	8.162*
60	8.370	5	8.155*
55	8.306	0	8.150*
50	8.243		

ALPHA PHASE			
0	7.8661	4	7.8638
1	7.8634	5	7.8647
2	7.8628	6	7.8658
3	7.8631		

by the National Youth Administration for making photometric measurements of the X-ray films.

SUMMARY

The results of an X-ray investigation of 15 iron-nickel alloys with a number of heat-treatments on each are reported.

The gamma-phase (face-centered cubic) alloy lattice constants were determined over the range 25 to 100 per cent nickel where this phase could be retained intact by drastic quenching. Positive deviations from the additivity rule of exceptionally high magnitudes were observed. The maximum lattice constant was found at about 39 atom. per cent nickel. From 100 to 43 atom. per cent nickel the lattice constant varies according to the equation:

$$a_0 = 3.64033 - 0.0012379 (\text{atom. per cent nickel})$$

It decreases sharply from its maximum value and from 0 to 20 per cent nickel it extrapolates in a linear manner to Öhman's value for pure gamma iron.

The alpha-phase range up to about 5 atom. per cent nickel was also studied and marked positive deviations found.

A limited number of experiments were made to determine the two-phase region in these alloys and highly tentative limits for this region are suggested in a diagram.

Experiments designed to verify or disprove the existence of compounds or superstructures (ordered atomic arrangements) in solid solutions are also reported. No indication of either was found.

A table of densities calculated from the lattice constants is included.

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13. G. Hagg: *Järnkontorets Annaler* (1934) **4**, 173.
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DISCUSSION

(John S. Marsh presiding)

M. L. FULLER,* Palmerton, Pa.—Some explanation of the departure of the lattice constants from that required by Vegard's rule might be forthcoming from studies of the X-ray emission spectra of alloys. As Dr. Jette has suggested, there may have been compound formation which the X-ray diffraction method did not detect.

We carried out some work of that kind some time ago, all of the results being negative. It is a particularly difficult thing to do with heavy metals because the electrons that are most likely to be affected by alloying or chemical combination are on the outermost electron shells. The corresponding spectra are of long wave lengths, requiring a difficult technique for measurement.

E. R. JETTE AND F. FOOTE (written discussion).—It will probably be difficult to investigate this problem by such methods. While both emission and absorption spectra of X-rays are known to change with chemical combination, the effects observed, even on light elements, are relatively small. The effects decrease with increasing atomic number. In a recent investigation Parratt¹⁹ determined the difference in the emission spectra of sulfur in the form of sulfates and of sulfides. The wave-length

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¹⁹ L. G. Parratt: *Phys. Rev.* (1936) **49**, 14.

shift was about 0.003\AA . Similar differences in absorption edges have been found by others²⁰ among sulfides of different metals. The effect is complicated and among the various factors that influence it are the screening effect of adjacent ions in the crystals, the sign of the ion (positive or negative), the distance between the ions, the screening effect of the electrons beyond the *K*-level and some characteristic properties of crystal itself. The main investigations on this effect have been concerned with ionic crystals. Only one investigation dealing with alloys has come to our attention. In this article, Parratt²¹ was dealing primarily with the widths of X-ray lines from alloy targets. In a footnote (p. 367) he observes that "the wave length differed with alloying, if at all, by less than 0.14 X.U. " (0.00014\AA). This was of the same order of magnitude as the experimental error. Unless special methods are devised, one of the greatest uncertainties in investigating the emission spectra of alloys is in the temperature of the particular portion of the target from which the X-rays are emitted. Occasionally we have melted iron targets when the X-ray tube was not operating correctly. The difficulties, arising from the temperature effect, in interpreting the results from the standpoint of compound formation, will be obvious to any metallurgist.

L. W. McKEEHAN,* New Haven, Conn.—I was particularly interested in the unsuccessful search for a superstructure and I was worrying about the straightness of the line showing the variation of parameter with composition. It has been proposed, I think, by H. J. Seemann, that an upward-bent line is a good clue to the existence of superstructures. Here there is a very straight line that is far too high at one end. The question is whether or not this is an exception to Seemann's tentative rule, that is, are we to consider the straight line as bowed up from the line joining 3 56 at the iron end to the nickel parameter, or are we to consider the straight line as indicating that in this region superstructures are not likely to be found?

The question is perhaps a little difficult to answer. I am sure it is difficult to formulate. If curvature in this sense is the critical thing, then one would expect to find special characteristics near the peak of the curve.

E. R. JETTE.—I think that what we know about the effect of superstructures on lattice constants at present will force us to leave the question open for the iron-nickel alloys. In a few cases where we have random distribution solid solutions at high temperatures but superstructures formed at lower temperature, it is found the average interatomic distance decreases somewhat when the superstructure is formed. This is observed in some cases but not in others.

The particular alloy on which we did quite a lot of work had the composition of FeNi_2 , where things seemed to happen. We annealed one sample for a long time at fairly high temperature (around 580°C.) and then we were a little uncertain whether the superstructure could form at that temperature, so we dropped back to about 450°C. It is true we got a somewhat lower lattice constant than at the higher temperature. The difference was about 15 in the fourth decimal place, which usually is beyond our experimental error, but the diffraction lines in the film for the low-temperature anneal, corresponding to annealing over two months, were still fuzzy. That meant the accuracy had dropped and we cannot be sure about the actual value of the lattice constants.

J. S. MARSH,† New York, N.Y.—I should like to suggest that the upward bend of the curve is not necessarily connected with superstructure.

²⁰ A. H. Compton and S. K. Allison: *X-rays in Theory and Experiment*, 667 et seq. New York, D. Van Nostrand & Co.

²¹ L. G. Parratt: *Phys. Rev.* (1935) **45**, 364.

* Director, Sloane Physics Laboratory, Yale University.

† Associate Editor, *Alloys of Iron Research*.

I suspect that Dr. Jette understated the case when he spoke of the "queer" behavior. The partial volumes of iron and nickel in the alloys, for example, will stir up things beautifully. These may be determined from the intercepts of the tangents of the specific-volume curve. Ordinarily, a positive volume-deviation curve is parabolic, consequently the plot of partial volumes is curved. The partial-volumes curves for iron and nickel, however, contain horizontal linear portions! So far as I know, there is no other example of such behavior.

The partial volumes, to be sure, merely show perhaps more spectacularly that which may be read from the lattice-constant curve; however, close inspection of data on many other properties shows that the unexpected is the rule of iron-nickel alloys.

The profession is indebted to Messrs. Jette and Foote for supplying reliable data where reliable data were needed badly.

R. M. BRICK, * New Haven, Conn.—A good many people publish designs of high-temperature cameras for X-ray work. Apparently in most cases the equipment is designed, a few photographs are taken and then the equipment is stored away. The limitations of these cameras are numerous. For one thing, it is necessary to avoid all changes of the surface structure or concentration due to the reaction with gases, such as oxygen. Also, it is impossible to work at temperatures at which the thermal activity of the atoms results in photograms unsuitable for analysis. A. J. Smith, of the Hammond Laboratory, has designed a camera with the furnace units separate from the film. The furnace unit itself is small and of simple construction. Several units could be built and specimens heat-treated until they are ready to be X-rayed. Equipment of that sort, it would seem to me, would be very suitable for studies on the iron-nickel alloys in determining the alpha plus gamma phase limits.

N. B. PILLING, † Bayonne, N.J.—Turn to Fig. 1, showing that curious twist in the curve of parameter versus composition. It follows a straight line down to 40 per cent nickel and hooks around in the way spoken of. This happens in the same range where all the curious physical properties occur. I wonder if it is at all feasible to think that this change is due to the beginning of a two-phase region. In the authors' heat-treatments the alloys were annealed to an equilibrium in the gamma phase and then quenched. Some of them entered the alpha plus gamma region and there is some opportunity for the initiation of change.

We can see from Figs. 4 and 1 that should some decomposition occur, with enrichment in nickel content of the residual gamma, the tendency would be toward a diminution of lattice constant in the mixture from that projected by the curve (Fig. 1).

E. R. JETTE.—I do not believe there is any chance that the alloys between 43 and 25 per cent are mixtures. That is one of the things we suspected in the beginning of the work and we took great pains to eliminate its possibility. Decomposition would show up in two ways. If the alpha phase appears at all, the gamma-phase lines are certain to be distorted and diffuse. Usually both sets of lines will be diffuse. If we look for these phases, not in the precision cameras but in cameras better suited to finding small quantities of any phase, the alpha phase would show up as extra lines. Again that did not happen. We believe we have eliminated the possibility of two phases in our alloys in this region beyond any doubt.

R. F. MEHL, ‡ Pittsburgh, Pa.—Whenever Dr. Jette speaks on the properties of solid solutions it seems to lead me to recall again work that I did some years ago on the

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‡ Director, Metals Research Laboratory, Carnegie Institute of Technology.

compressibility of solid solutions²². The measured compressibility of the alloy Invar is much higher than that calculated from the compressibilities of alpha Fe and Ni, and would imply an unbelievably high compressibility of gamma Fe. The measurements by Dr. Jette show abnormally high values of the lattice parameter, equivalent to densities much lower than the rule of mixture values. This low density is consistent with the high compressibility observed, for compressibility is inversely related to density.

S. EPSTEIN,* Columbus, Ohio.—Might not the fact that the gamma-alpha iron change is brought down to room temperature at the composition 30 per cent nickel have something to do with the shape of the curve? If that is so, would it not be well to study an analogous system? We know that in the iron-manganese system, the change from gamma to alpha is similarly brought down to room temperature. Would not that be a means of testing whether it is the lowering of the gamma-alpha change or something else that gives the bulge in the curve?

It has been suggested that the anomaly in the coefficient of expansion in the iron-nickel system may be due to the fact that in the anomalous composition region the magnetic change is suppressed to room temperature, and is raised again above room temperature for higher nickel contents. With manganese that explanation would not hold because manganese is itself not a magnetic element, as nickel is.

Thus studies on the iron-manganese system would be a nice way of checking the validity of the theory that the magnetic inversion is the cause of the anomaly in the iron-nickel system.

F. M. WALTERS,† Youngstown, Ohio.—There is no anomaly of expansion of the Invar type in the binary iron-manganese alloy. At the compositions at which such an anomaly might be expected, gamma decomposes to the close-packed hexagonal phase gamma. Of the phases occurring in the iron-manganese system, only alpha is magnetic.

J. S. MARSH.—If a compound is ever found in iron-nickel alloys the finding will be contrary to human experience so far. That large, positive deviations are associated only with tendency to break into two phases is clear, I think.

S. EPSTEIN.—Would you attribute the low coefficient of thermal expansion to the magnetic change?

J. S. MARSH.—I believe it is tied up with the fact that Invar at room temperature happens fortuitously to be in the range of largest change of specific heat; most of the heat input goes to demagnetize the alloy.

S. EPSTEIN.—You associate this anomaly in the iron-nickel system with the change in magnetic properties in that composition region?

J. S. MARSH.—Yes.

E. R. JETTE.—The question of whether there are compounds in this system and what their compositions might be has come up several times during this discussion. We purposely stayed away from speculation on possible compounds and things of that general nature; not that we have not tried to find compounds but every attempt has been entirely unsuccessful. Both of these elements are transition elements and in the

²² R. F. Mehl and B. J. Mair: Chemical Affinity in Metallic Alloys, Especially Solid Solutions: A Study in Compressibility. *Jnl. Amer. Chem. Soc.* (1928) **50**, 55.

* Metallurgist, Battelle Memorial Institute.

† Research Engineer, Youngstown Sheet & Tube Co.

Hume-Rothery classification of intermetallic compounds both would have zero valences. And then we find some of the magnetic properties have minima at around 30 per cent and maxima at 50. Others show curious behaviors around FeNi_2 , still others near the composition FeNi_4 . It seems quite certain that a compound cannot be found for every maximum or minimum in the single properties. If you sum up all the properties, you will be confronted with the question: What property does indicate compound formation? I do not know, so the question has been dodged all the way through, and we much prefer to present this material as data on which others concerned with magnetic phenomena can base calculations and work of their own.

E. R. JETTE AND F. FOOTE (written discussion).—Dr. Epstein's points were left unanswered at the time of the meeting, owing to lack of information. It is difficult to see, in the light of our present knowledge, how the shift in the temperature of the gamma-alpha change could influence the sizes of the atoms that are the primary factors in determining lattice constants. Remembering, however, that our actual measurements were made at room temperatures, and that so little is known about the rate of change of lattice constant with composition at different temperatures, anything we might say on this point would be pure speculation.

As far as can be determined, there is little similarity in the behavior of the lattice constant vs. composition curves of the Fe-Ni and Fe-Mn systems for the face-centered cubic structures. Using the data of Öhman (ref. 12) we find that from 15 to 65 atomic per cent manganese the plot is a straight line. It extrapolates to a value for gamma iron that has been checked by Hagg (ref. 13) on the iron-carbon alloys.

Since manganese exists in three forms, three distances of closest approach of atoms are found, which may be used for determining whether the deviations from Vegard's rule are positive or negative. Since there is a close relation between the face-centered cubic structure of gamma iron and the face-centered tetragonal structure of gamma manganese, we have used the latter to obtain the ideal or Vegard's rule curve. This value of the atomic radius is incidentally the largest of the three²³ but even with this value pronounced positive deviations are observed which are linear up to the limiting composition of the gamma iron phase. It might be possible to prove that the deviations are negative if the atomic radius obtained from beta manganese were used with a factor to compensate for the difference, if any, of coordination number (ref. 15). The coordination number for beta manganese is not known, and the factor by which the radius would need to be multiplied is so uncertain that we shall not discuss the possibility further.

²³ M. C. Neuberger: *Ztsch. f. Krist.* (1933) **A86**, 395.

Preferred Orientations Produced by Cold-rolling Low-carbon Sheet Steel

BY M. GENSAMER* AND R. F. MEHL,* MEMBERS A.I.M.E.

(New York Meeting, February, 1936)

ALTHOUGH a large number of X-ray photograms of cold-rolled steel have been published, two circumstances have led to the experimental work reported in this paper. The first is that no complete study, making use of the pole-figure method of Wever¹, has been made of cold-rolled low-carbon steel. Wever has published pole figures of mild steel subjected to plane parallel deformation^{1,2} and undoubtedly he has applied the method to cold-rolled mild steel, but the authors have not found these data published. Kurdjumow and Sachs³ have applied the method to the study of rolling and recrystallization textures in electrolytic iron; their results will be referred to later. The reason for this dearth of papers using the pole-figure method is obvious; a greater number of photograms and more analytical work (although this work is quite simple and straightforward) are required to construct a pole figure than most investigators have felt worth while, despite the fact that no other method of which the authors are aware will satisfactorily depict the orientations of the crystallites in a polycrystalline aggregate.

The second circumstance that led to the work reported in this paper was the appearance of a paper by Wayne A. Sisson⁴ on the same subject. In his valuable study of the factors influencing the development of preferred orientations in cold-rolled mild steel, Sisson made one observation that required confirmation; that is, that at some stage of the rolling process the type of preferred orientation changed from the type that gives a photogram characterized as a "six-point" X-ray pattern to that known as a "four-point" pattern. A similar observation had been made by Tammann and Heinzel⁵, who studied the orientations developed in the rolling of steel by the specular reflection of light from the etched surface of rolled samples. These workers also found that the type of preferred orientation changed during the rolling process. The authors had some difficulty in seeing how this behavior could be consistent with modern views on the genesis of preferred orientations, particularly with those of Wever²

Manuscript received at the office of the Institute March 2, 1936.

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and of Boas and Schmid⁶. It seemed, in view of the now well-known phenomenon of zonal textures in rolled sheets (see the work of Vargha and Wassermann on rolled aluminum sheets⁷), that both Sisson and Tammann and Heinzel might have encountered this behavior in iron and mistaken it for a change in type of preferred orientation with progressive rolling.

The objectives of this work were then: (1) to study this supposed change in type of preferred orientation with rolling, and (2) to describe completely by means of pole figures whatever orientations might be found.

A supply of automobile body sheet bar was obtained, $\frac{1}{4}$ in. thick, which had had standard mill processing up to this point. It was then given three consecutive normalizing treatments in a continuous normalizing furnace operating at 1850° F. (1010° C.) and a speed of 8 ft. per min. The bars probably reached 1750° F. (950° C.). A bar was straightened and then annealed at 1000° C. and cooled in the furnace. It was realized that this would produce a large initial grain size, but a material as free as possible from directional properties was desired. The bar was then accurately ground to a thickness of 0.200 in. and a width of $3\frac{3}{8}$ in. and rolled in 35 passes to a thickness of 0.010 in., a reduction of 95 per cent in thickness and cross-section area, taking samples every 5 per cent beyond 30 per cent reduction. Since Sisson's work seems to have shown conclusively that tension applied during rolling does not affect the degree or type of orientation developed, tension was applied in reducing the steel from 0.020 in. to 0.010 in. to prevent curling. A four-high mill was used up to this point, the working rolls of which were 2 in. in diameter. The 0.010-in. thick sheet was then rolled on a two-high mill with rolls $2\frac{3}{8}$ in. in diameter without tension to 0.002 in. thick in a great many passes, taking a sample at 0.005 in. During all this rolling the direction of rolling was frequently reversed.

There were thus available samples cold-rolled from 30 to 95 per cent at 5 per cent intervals as well as samples cold-rolled 97.5 per cent and 99 per cent of mild rimmed steel of the following analysis: C, 0.05 per cent; Mn, 0.34; P, 0.010; S, 0.020; Si, 0.004; Cu, 0.044; Ni, 0.025 and Cr, 0.036. From these samples specimens were prepared for X-ray study. They were so cut that the region studied would be about $\frac{3}{4}$ in. from the edge of the sheet. Specimens that were to represent the inside of the sheet were prepared by milling and grinding off an exactly equal amount from both surfaces of the sheet, while for the outside or surface-layer specimens, all the milling and grinding was done from one side. Milling was not carried below a thickness of about 0.030 in. The grinding operation was carried out slowly with a strong stream of water on the specimen, using a surface grinding machine and with the specimen mounted on a microscope slide glass with bakelite resinoid varnish baked on at 105° C. It is not likely that the *average* temperature exceeded this at any time during rolling or afterward. After rough grinding to about 0.010 in.

the specimens were alternately smoothed by hand on metallographic polishing paper and etched, removing each time about 0.001 in. by polishing, then etching for 5 min. in warm dilute HCl. The final thickness after the last etching was 0.10 mm., or 0.004 inch.

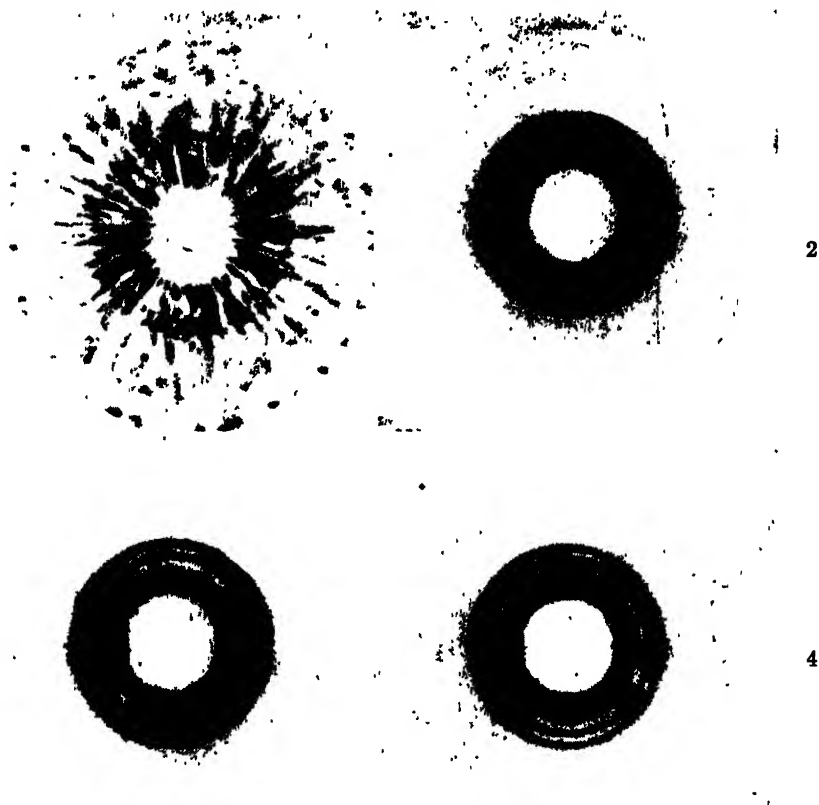


FIG. 1.—BEAM 90° TO SURFACE, SAMPLE REDUCED 0 PER CENT

FIG. 2.—BEAM 90° TO SURFACE, SAMPLE REDUCED 60 PER CENT, INSIDE OF SHEET.

FIG. 3.—BEAM 90° TO SURFACE, SAMPLE REDUCED 60 PER CENT, OUTSIDE OF SHEET.

FIG. 4.—BEAM 90° TO SURFACE, SAMPLE REDUCED 80 PER CENT, INSIDE OF SHEET.

A pinhole photogram was made of each of these specimens, using a pinhole 1.0 mm. in diameter and 25 mm. long and with the specimen 5 cm. from the film. About 5 hr. was required using a Mo target at 35 kv. and 20 ma. Some of these photograms are reproduced in Figs. 1 to 14. In each case the X-ray beam is perpendicular to the rolling plane and the rolling direction is vertical.

Fig. 1 shows how large was the initial grain size in these experiments, and accounts for the relatively large amount of rolling required to produce

280 ORIENTATIONS PRODUCED BY COLD-ROLLING LOW-CARBON SHEET STEEL

a well defined fiber pattern in this work as compared with that of Sisson and others. There were by grain count on a representative photomicrograph about 400 grains per sq. mm. (between A.S.T.M. grain-size numbers 5 and 6).

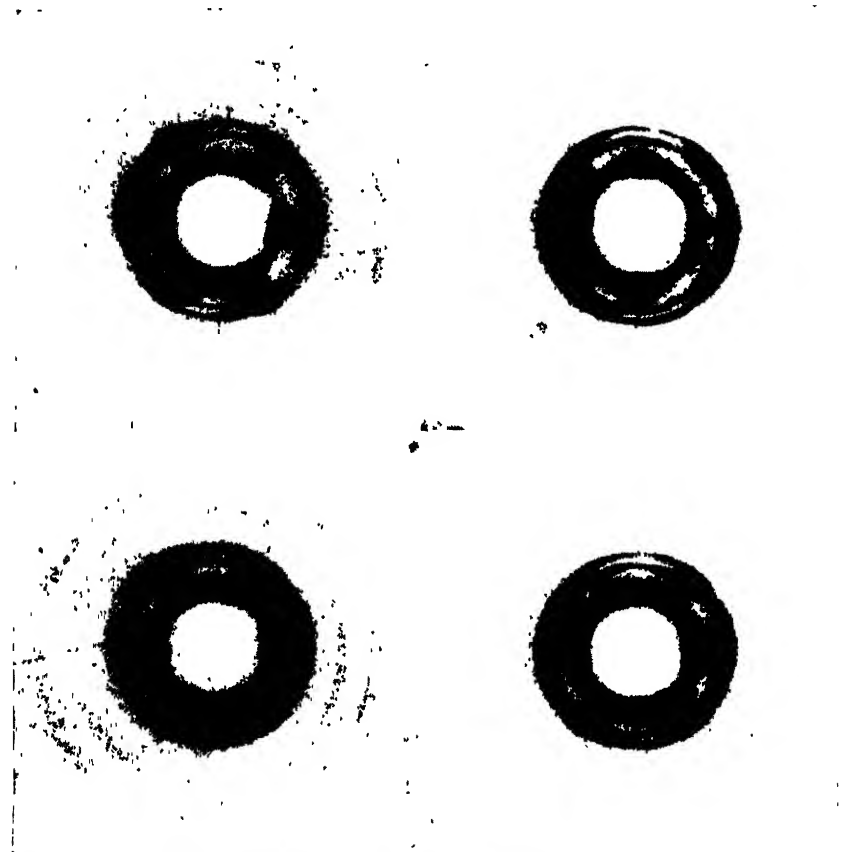


FIG. 5.—BEAM 90° TO SURFACE, SAMPLE REDUCED 80 PER CENT, OUTSIDE OF SHEET.
FIG. 6.—BEAM 90° TO SURFACE, SAMPLE REDUCED 85 PER CENT, INSIDE OF SHEET.
FIG. 7.—BEAM 90° TO SURFACE, SAMPLE REDUCED 85 PER CENT, OUTSIDE OF SHEET.
FIG. 8.—BEAM 90° TO SURFACE, SAMPLE REDUCED 90 PER CENT, INSIDE OF SHEET.

Traces of preferred orientation can be detected with less cold-rolling, but it was not until 40 per cent reduction that a well defined fiber pattern developed in these photograms. At this stage the photograms were still spotty, owing to the large initial grain size. At 60 per cent reduction the fiber patterns were quite well developed, although fragmentation had not occurred to an extent sufficient to give continuous Debye rings. (It must not be assumed that continuous Debye rings indicate complete fragmentation.) Figs. 2 and 3 are the inside and outside, respectively, of

the sample reduced 60 per cent. At the point where a well defined fiber pattern was first developed, the inside and outside layers gave photograms of different types. The inside of the sheet was developing a "four-point" pattern and the outside a "six-point" pattern.

At 80 per cent reduction, Figs. 4 and 5, this difference was more pronounced, for the fiber patterns were better developed, and it persisted

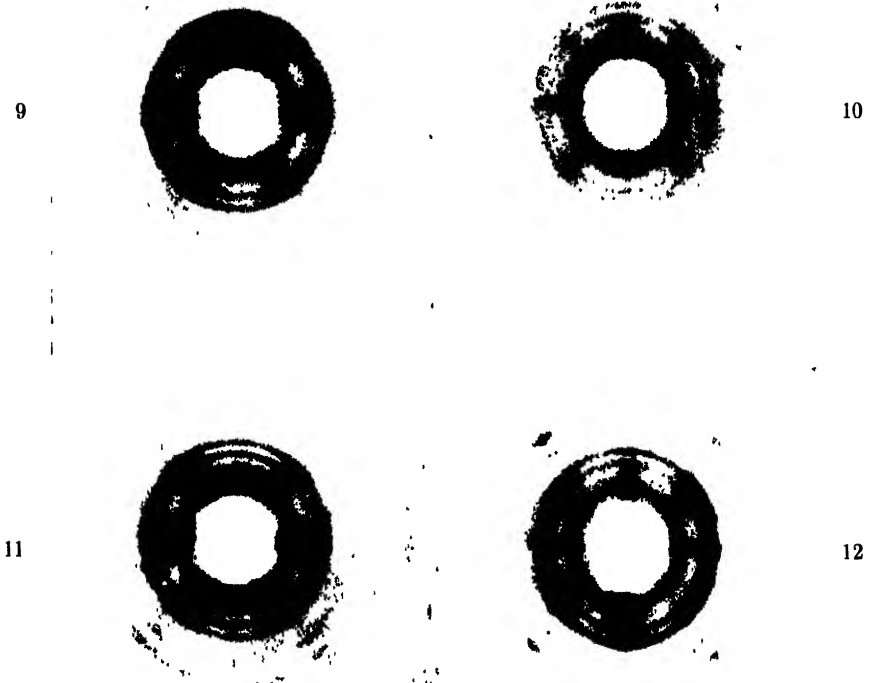


FIG. 9.—BEAM 90° TO SURFACE, SAMPLE REDUCED 90 PER CENT, OUTSIDE OF SHEET.
FIG. 10.—BEAM 90° TO SURFACE, SAMPLE REDUCED 95 PER CENT, INSIDE OF SHEET.
FIG. 11.—BEAM 90° TO SURFACE, SAMPLE REDUCED 95 PER CENT, OUTSIDE OF SHEET.
FIG. 12.—BEAM 90° TO SURFACE, SAMPLE REDUCED 97.5 PER CENT, INSIDE OF SHEET.

through 95 per cent reduction, illustrated in Figs. 6 to 11, of which Figs. 6, 8 and 10 are the inside of the sheet and Figs. 7, 9 and 11 the outside. Beyond 95 per cent the samples were too thin to permit the preparation of a specimen from the outside layer, and Figs. 12 and 13, inside and outside respectively of the sample rolled 97.5 per cent, both had the "four-point" pattern typical of the inside of the sheet.

Now if observations were confined to samples prepared by removing most of the metal from one side only, and thus in the thicker samples to study the outside layers and in the thinner samples to study the inside zone (because the relatively thin outside zone is removed by etching), it would be concluded that the type of preferred orientation developed changes at some stage of the rolling from one type to the other. The authors suspect that this is what happened in Sisson's studies. It is almost certainly the case in Tammann and Heinzel's work, for they removed only a shallow layer from the surface by etching, since the



FIG. 13.



FIG. 14.

FIG. 13.—BEAM 90° TO SURFACE OF SAMPLE REDUCED 97.5 PER CENT, OUTSIDE OF SHEET.
 FIG. 14.—BEAM 90° TO SURFACE OF SAMPLE REDUCED 99 PER CENT, INSIDE OF SHEET.

"glimmer" method used by them does not require the preparation of thin sections.

Description of a fiber pattern as a "four-point" or a "six-point" type is not a complete description of the orientations of the crystallites in an aggregate in which preferred orientations are exhibited. Neither is a description of the texture in terms of one or more ideal orientations a complete story. To do this most conveniently requires the use of Wever's method of pole figures, by which the orientations present are represented through the stereographic projection of the poles of a family of crystallographic planes. The method will not be described here in detail, because Wever has done this quite adequately in an American publication².

The authors have chosen to represent the orientations present in their samples through the projection of the poles of the $\{110\}$ planes, making use of the reflections from these planes of both white and characteristic radiations from a Mo target at 35 kv., with the same set-up used to obtain the photograms of Figs. 1 to 14. In these photograms the inner-

most and most intense Debye ring is produced by white radiation from the $\{110\}$ planes, the next ring is produced by the $\{110\}$ planes and the K_β radiation, and the third by the $\{110\}$ planes and the K_α radiation. The first and third rings have been used in this work. At the voltage used, the average value of θ in the first case is about 7° , and in the case of the K_α line it is about 10° . In addition to the advantage associated with the relative intensity of these reflections, fewer photograms are necessary satisfactorily to sweep over the whole stereographic circle.

Photograms were made with each specimen rotated about the rolling direction in one way only in 5° steps from 0° to 70° , and 5° both ways about an axis in the plane of rolling and perpendicular to the rolling direction, which hereafter will be known as the transverse direction. After 45° rotation about the rolling direction, the specimens were polished down to a wedge shape and mounted with the sharp edge of the wedge in the path of the beam, and exposures continued, using two films in the cassette, to a rotation of 70° , and in some cases to 75° .

The construction of a pole figure from these photograms calls for a very careful comparison of the intensities of all points on the chosen Debye ring in all the photograms. An effort was made to keep all the exposures the same, which requires some adjustment of time as the sample is rotated away from the normal position. Plotting was facilitated by the use of a chart constructed as described in Wever's paper. Such a chart is prepared by rotating the reflection circle (which is the stereographic locus of normals to all the planes that can reflect a beam of X-rays of a particular wave length) into the projection plane, through the same number of degrees through which the specimen had been rotated away from the plane of the film in making each exposure. The procedure followed in plotting the data was to estimate the relative intensity around the chosen Debye ring on each photogram, then transfer the data directly to the chart. This results in a pole figure for which the plane of projection is the rolling plane. The reflection circle for α iron $\{110\}$ reflection of white radiation, for which $\theta \cong 7^\circ$ in this work, and for 0° rotation of the specimen, is shown in Fig. 16 by the dotted circle; the dotted circle in Fig. 17 is the corresponding reflection circle for the reflection of Mo K_α radiation, for which $\theta \cong 10^\circ$. Since the rotation of the specimen was in one manner only about the rolling direction, it was necessary, in order to complete the pole figure, to make use of the fact that in rolling there must be a plane of symmetry perpendicular to the rolling plane and containing the rolling direction. This is the only assumption of any kind involved in the preparation of these pole figures, and could be eliminated by repeating the whole process, rotating the specimen about the rolling direction in the opposite way. The assumption of this symmetry plane is perfectly valid, however, and nothing would be gained by these additional expo-

tures; this was proved in several cases by rotating the specimen 180° about the normal to the plane of rolling as an axis with no change in the resulting photogram.

The first specimen selected for a complete pole-figure study was the most severely cold-worked one, which had 99 per cent reduction of area

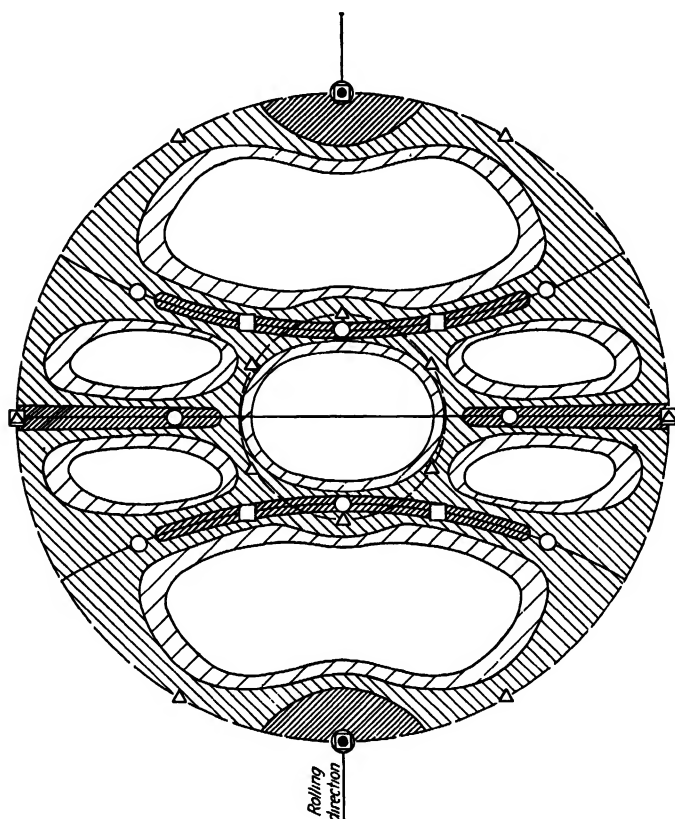


FIG. 15.— $\{110\}$ POLE FIGURE FOR SAMPLE REDUCED 99 PER CENT BY COLD ROLLING.

- and ——— indicate simple tension texture with rolling direction as axis.
- — — indicates simple compression texture with normal to sheet as axis.
- shows $\{110\}$ as rolling direction, $\{100\}$ as rolling plane.
- shows $\{110\}$ as rolling direction, $\{112\}$ as rolling plane.
- △ shows $\{112\}$ as rolling direction, $\{111\}$ as rolling plane.

by rolling to a thickness of 0.002 in. The photogram obtained with the beam perpendicular to the surface of the sheet is reproduced in Fig. 14. It is typical of the inside of the sheet specimens that had suffered less reduction, but in it the fiber structure is better developed. The pole figure prepared from the data obtained by the analysis of 18 photograms each at a different angle of incidence of the X-ray beam on the surface of the sheet is reproduced in Fig. 15. In this diagram the plane of rolling

is the projection plane and the rolling direction is indicated; the heavily shaded areas represent the stereographic regions of most frequent occurrence of orientations of $\{110\}$ planes, the lightly shaded areas are regions of less frequent occurrence (areas of moderate to very light darkening of the X-ray films), and the blank areas are regions of orientation completely absent from this specimen as far as can be determined by lack of perceptible darkening of an X-ray film under the conditions

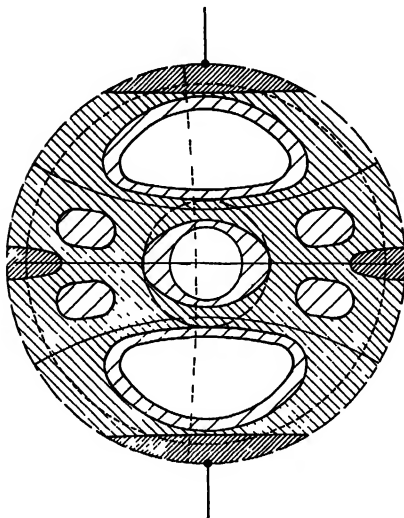


Fig. 16.

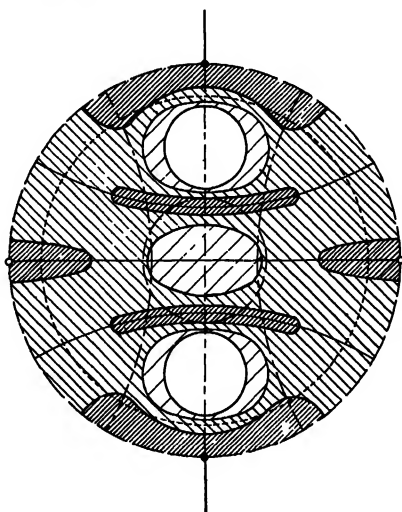


Fig. 17.

Fig. 16.— $\{110\}$ POLE FIGURE FOR INSIDE OF SHEET REDUCED 85 PER CENT BY COLD-ROLLING.

- and — indicate simple tension texture with rolling direction as axis.
- — — indicates simple compression texture with normal to sheet as axis.
- — — shows reflection circle for white radiation incident normal to the sheet.
- — — — — shows reflection circle for white radiation incident in the trans-

verse direction

Fig. 17.— $\{110\}$ POLE FIGURE FOR OUTSIDE OF SHEET REDUCED 85 PER CENT BY COLD-ROLLING.

- and — indicate simple tension texture with rolling direction as axis.
- and — — — — — indicate simple tension texture with transverse direction as axis.
- — — shows reflection circle for $M\alpha K\alpha$ radiation incident normal to the sheet.
- — — indicates simple compression texture with normal to sheet as axis.

prevailing in these experiments. This is nearly a complete representation of the existing orientations. It could be improved by the use of contours or lines of constant frequency of occurrence instead of a simple division of the reflection circle into regions of only four degrees of relative frequency, but such a procedure would require the use of a microphotometer and a greatly refined technique not considered worth while at this stage of the study of deformation textures. The other features of this diagram will be described later.

Figs. 16 and 17 are the diagrams prepared from a similar analysis of specimens from the inside and outside zones, respectively, of the sample

rolled 85 per cent. This sample showed the most pronounced difference between the inside and outside zones in a simple pinhole photogram (Figs. 6 and 7). At this stage of rolling the fiber texture was not sufficiently well developed to give a pole figure with such well defined regions as the one for the material cold-rolled 99 per cent. Yet it may be seen that Figs. 16 and 17 are very similar to Fig. 15. The most pronounced difference between the inside and outside zones of the sample reduced 85 per cent seems to be a somewhat different distribution of the regions of relative frequency of occurrence of $\{110\}$ planes, rather than a rotation of the one with respect to the other. To discuss this difference, it will be necessary to consider in greater detail the significance of the pole figure for the sample reduced 99 per cent (Fig. 15).

On the diagram of Fig. 15 there are also indicated the ideal orientations of Kurdjumow and Sachs for electrolytic iron and the simple tension and compression orientations made by Wever to account for the cold-rolling texture of iron. The three ideal orientations of Kurdjumow and Sachs are represented by small squares, circles and triangles. The squares would be the ideal poles of the $\{110\}$ planes if all the crystallites were so oriented that a $[110]$ direction were parallel to the rolling direction and a $\{100\}$ plane were parallel to the rolling plane. The circles correspond to the case of a $[110]$ direction as the rolling direction and a $\{112\}$ plane as the rolling plane, and the triangles to the case of a $[112]$ direction as the rolling direction and a $\{111\}$ plane as the rolling plane.

Kurdjumow and Sachs offered no mechanism of genesis of these ideal orientations, but it may be seen how well they fit the experimental data and account for all the orientations present. The principal weakness of this method of accounting for the observed orientations is its failure to account adequately for the region of moderate intensity completely encircling the pole figure at its periphery. It is difficult to see how scattering about the ideal orientations could give this feature of the pole figure.

Wever proposed to account for the observed rolling texture by considering it to be the result of simultaneous flow in compression in a direction perpendicular to the rolling plane and in tension in the rolling direction. Boas and Schmid⁶ have shown how the simple tension and compression textures can be predicted from the way in which the orientation of a single crystal will rotate under the action of the stress field characteristic of each of these processes into a stable orientation that is dependent on the original orientation of the crystal. These stable orientations are represented in Fig. 15 by solid lines and filled-in circles for flow in tension in the rolling direction, and by dashed lines for flow in compression in the direction perpendicular to the surface of the sheet. Wever's hypothesis is

simply that the rolling texture is one that is consistent with both these ideal textures, since the deformation produced in rolling can be considered to be brought about by the combined action of a flow as in tension in the rolling direction and a flow as in compression normal to the rolling plane. That this picture of the process is fairly consistent with the orientations developed may be seen in Fig. 15 by comparing the cross-hatched regions, which were obtained experimentally, with the regions predicted by the theory, represented by the solid circles and lines for tension and the dashed lines for compression. It is the opinion of the authors that Wever's point of view is superior in this case to that of Kurdjumow and Sachs, but it is not yet a complete description of the process. The tension texture developed is limited. To show that this is so, we may adduce the observation that the horizontal solid line of Fig. 15, which bisects the circle and which should be the center of a region of high frequency of occurrence of $\{110\}$ poles throughout its length if a simple tension texture existed, runs through a region at the center of the diagram devoid of observed $\{110\}$ poles; similarly, the solid lines above and below this middle line run through regions of only moderate frequency near the periphery of the circle. The ideal compression texture is more nearly consistent with observation. This limitation to the developed tension texture adds weight to the existence of Kurdjumow and Sachs' ideal orientations as equilibrium orientations, but we have as yet no exposition of their genesis.

An explanation for the limited tension texture observed in rolled iron may come from a close study of the limitations to flow in the rolling process; since there is no widening of the sheet, the slip systems that result in a change of transverse dimensions should be used *least*, which is equivalent to saying that there should be a minimum of rotation of the crystals about both the normal and rolling directions, with considerable rotation about the transverse direction. It is impossible for rotation to be completely restricted to the transverse direction as an axis, since the rotation axis for each crystal is presumably determined by the orientation of that crystal; but since at least 12 slip systems are operative in body-centered cubic iron (and many more if Gough is right that $\{110\}$, $\{112\}$ and $\{123\}$ planes may be used) it is possible that every crystal might rotate only about an axis that is a close approximation to the transverse direction. The exactness of this choice is again restricted, however, by the variation in stress field from grain to grain, which must be produced by both the elastic anisotropy of iron and the local disturbances arising from the lack of cooperative slip between adjacent grains. It is not thought advisable to pursue further the theoretical study of the process at this time, as such a study would involve the calculation of resolved shear stresses in all the possible slip systems and for all orientations, a quite formidable task in itself and of doubtful value until

more is known about the crystallographic mechanism of slip in iron. It is hoped that the study of the deformation of single crystals of iron which this laboratory has undertaken will make the solution of the problem possible.

Turning to the difference between the textures developed by the inside and the outside of the sheet (shown in Figs. 16 and 17), the problem becomes still more difficult. It was thought for a time during this study that the texture of the outside of the sheet might be explained by a rotation of the presumably normal texture of the inside of the sheet about the transverse axis. Completion of the pole figures gave no confirmation of

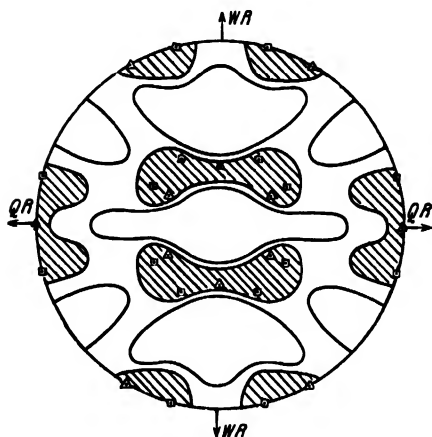


FIG. 18.—KURDJUMOW AND SACHS' $\{110\}$ POLE FIGURE FOR COLD-ROLLED ELECTROLYTIC IRON RECRYSTALLIZED BETWEEN 550° AND 840° C.

this hypothesis. One possible interpretation is that in addition to the tension and compression textures described above, and which seem to explain well enough the data for the inside of the sheet, there exists in the outside of the sheet a tendency toward an ideal tension texture which has the transverse direction for its axis. This ideal texture is shown by the dash-dot lines and open circles of Fig. 17. (The solid circles and lines and the dashed lines have the same significance in Figs. 15, 16 and 17.) If this is the explanation, it means that grains located near the surface of the sheet have a

greater freedom in the choice of a slip system than inside grains.

Another explanation for the difference between the inside and outside of the sheet is suggested by the work of Kurdjumow and Sachs³ on the recrystallization texture of electrolytic iron. Fig. 18 is their $\{110\}$ pole figure for cold-rolled electrolytic iron that had been recrystallized by annealing for 20 min. at any temperature between 550° and 840° C. Careful comparison of this pole figure with those of Figs. 16 and 17 will reveal that the superposition of the pole figure of Fig. 18 (recrystallization texture) on the pole figure of Fig. 16 (normal texture or texture of inside of sheet) might very well produce a pole figure similar to that of Fig. 17 (texture of outside of sheet). This suggests that the texture of the outside of the sheet may be produced by partial recrystallization of the outside zone, caused by temperatures exceeding the recrystallization temperature. Not only may the outside temperatures be higher for a limited period of time, but the recrystallization temperature may be lowered by a greater degree of cold-work on the outside caused by roll friction. This seems a

quite plausible explanation to the authors and, for the present, superior to that offered in the last paragraph.

One other point in connection with these pole figures should be mentioned. N. P. Goss, in a paper as yet unpublished, has called attention to the greater sensitivity, to low degrees of cold-work, of photograms prepared with the X-ray beam traversing the specimen in what the authors have called the transverse direction and which he proposes to call the principal direction (a nomenclature that seems unwise to the authors). That photograms so prepared will have diffraction rings with more pronounced maxima and minima is quite true, and the reason for it is obvious from the pole figures of Figs. 15 and 16. In Fig. 16, the reflection circle for white radiation, shown by the dotted circle near the periphery, has been rotated 90° (corresponding to 90° rotation of the specimen, or transmission of the beam in the transverse direction), and in this rotated orientation it is represented by the interrupted dotted line (the nearly vertical line of Fig. 16). Scrutiny will show that in this orientation the reflection circle traverses regions of high intensity six times, and between these traverses regions of very low intensity, giving rise to a well developed six-point fiber pattern, whereas the reflection circle corresponding to normal incidence of the X-ray beam (the uninterrupted dotted circle) traverses regions of high intensity only four times, and between these traverses no regions of low intensity but only regions of moderate intensity, giving rise to a less well developed four-point fiber pattern. In this paper Goss reports some results with hot-rolled steel rods which indicate a different type of preferred orientation from that developed by cold-drawing. It is hoped that someone will have an opportunity to study these hot-working textures by the pole-figure method and elucidate their genesis, particularly to see what relation, if any, they bear to the recrystallization textures of Kurdjumow and Sachs³.

SUMMARY

1. It has been shown that in the cold-rolling of mild steel the preferred orientations develop gradually, approaching more nearly a state of complete orderliness of orientation of all the crystallites. There is no change in type of preferred orientation (that is, from six-point to four-point fiber diagrams) during the course of rolling.

2. It has been shown that a zonal texture exists in cold-rolled mild steel with the outside layer exhibiting a modification of the texture (preferred orientations) developed at the center of the sheet. The texture of the outside of the sheet gives rise to a six-point diagram in a normal pinhole photogram, whereas the inside of the sheet produces a four-point diagram.

3. Pole figures have been prepared for these textures, resulting in a nearly complete description of the orientations developed and clearly

showing the nature of the difference between the inside and the outside zones. These textures cannot be described in any simpler or clearer way than by the use of stereographic pole figures.

4. These pole figures indicate that the texture developed for the inside of the sheet is the same as that described by Kurdjumow and Sachs and elucidated further by Wever. Wever's explanation, in terms of superposition of simple tension and compression textures, seems to account adequately for this texture, and it is particularly satisfactory because it agrees well with what we know about the crystallographic mechanism of translation or slip and the rotation accompanying slip in single crystals, as has been pointed out by Schmid and Boas. The texture for the outside layers of the sheet is not to be explained so simply. The conditions during rolling that give rise to these differences between the outside and inside need to be explained, and it is hoped that the greater understanding of the rolling process that will explain these differences will lead to practical developments.

ACKNOWLEDGMENT

The authors wish to acknowledge the competent and enthusiastic assistance of R. H. Schaefer, now with the International Nickel Co. at Bayonne, N.J., and formerly assistant in the Metals Research Laboratory, Carnegie Institute of Technology, in preparing the specimens and making the X-ray photograms for this paper.

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DISCUSSION

(John S Marsh presiding)

S EPSTEIN,* Columbus, Ohio.—I did not hear the degree of work that can be recognized by these pole figures. About the least amount of cold-work that can be recognized in the microscope is 30 per cent. What is the least amount of cold-work that can be recognized by this method?

M. GENSAMER.—A good bit less than 30 per cent, particularly using the transverse direction. However, notice Fig. 2, for 60 per cent reduction. This is not typical, but is a very coarse-grained structure. In finer grained steel it would show up earlier. I think we can beat 30 per cent even in this coarse structure.

* Metallurgist, Battelle Memorial Institute.

F. M. WALTERS,* Youngstown, Ohio.—Mr Goss, of the Cold Metals Process Co., has been able to detect less than one per cent of cold-work.

M. GENSAMER.—That depends upon the grain size you start with.

J. T. NORTON,† Cambridge, Mass.—How did you get around the difficulties of the really coarse-grained materials?

M. GENSAMER.—We did not attempt to apply pole figures. The first one for which we made a pole figure inside and outside was a specimen reduced 85 per cent.

J. T. NORTON.—Did you measure the intensity of these parts of the reflected beams?

M. GENSAMER.—All we did was to measure by eye, and I think that is satisfactory. It gives all the information we used at this stage.

J. T. NORTON.—Did you estimate three or four degrees of intensity?

M. GENSAMER.—Four degrees of intensity—practically none, weak, medium and strong. If we could use a densimeter and could plot something more nearly absolute, we could make the pole figures contour maps, but I do not think we need to do that yet.

S. EPSTEIN.—I am confessing a great deal of ignorance about this, but what is determined when a different pole figure is obtained for cold-worked than for unworked material? Obviously the preferred orientation after cold-work makes the main difference, but does the strain produced by cold-work also influence the pole figure?

M. GENSAMER.—For unworked material, that whole pole figure would be uniform. It would be completely filled in because grains of all orientations are present. The fact that certain regions are blank indicates that there are no grains of such orientation.

S. EPSTEIN.—The pole figures give no indication of the strains produced?

M. GENSAMER.—Not by this method.

N. B. PILLING,‡ Bayonne, N.J.—I wonder if there are not others like myself, who would appreciate a demonstration of the structures you are dealing with

M. GENSAMER.—If we had only one ideal preferred orientation present in the cold-rolled sheet, let us say the one that formerly we thought to be the only one present, in which the elementary cubes are lined up so that a cube plane is in the plane of rolling and a $[110]$ direction is lined up in the rolling direction, Fig 79 in Jeffries and Archer's "Science of Metals," reproduced herewith as Fig. 19, would describe it. I cannot draw a picture of the textures as actually present. There is a considerable range of orientations.

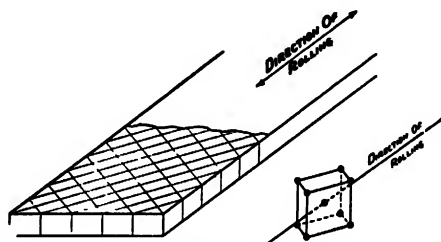


FIG. 19.—PREFERRED ORIENTATION OF CRYSTAL FRAGMENTS IN SEVERELY ROLLED SHEET OR FOIL OF METAL CRYSTALLIZING WITH BODY-CENTERED CUBIC SPACE LATTICE. (From *The Science of Metals*, by Zay Jeffries and R. S. Archer. McGraw-Hill Book Co.)

N. B. PILLING.—You show two prevailing differences between the center and the outside.

* Research Engineer, Youngstown Sheet & Tube Co.

† Associate Professor, Physics and Metals, Massachusetts Institute of Technology.

‡ Manager, Research Laboratory, International Nickel Co.

M. GENSAMER.—I cannot describe that as simply. That is the real advantage of the pole-figure method. A person familiar with the method can tell at a glance what the differences are.

M. L. FULLER,* Palmerton, Pa.—Dr. Norton has raised the question as to what one would do in determining orientations in coarse-grained material. That can be handled quite well if one has a mechanism for moving the specimen continuously during the course of the exposure, all the while preserving the specimen in the same plane and the same direction with respect to the X-ray beam. We have done that successfully with coarse-grained zinc.

R. F. MEHL.—In the course of the preliminary symposium on X-ray methods in the testing of materials held by the American Society for Testing Materials, in Detroit last year, some six persons related their "discovery" of the method for studying preferred orientation in large-grained specimens by using devices to move the sheet transversely during exposure; we now have a seventh!

Papers like this usually need a little general explanation, for the subject seems abstruse, the methods complicated, and the purpose uncertain, if not useless. The first and most important objective is the description of the mechanism by which preferred orientations are generated on cold-working; this necessarily involves a consideration of mechanisms of slip in single crystals and the part these mechanisms play in special types of deformation of aggregates. The second objective is the determination of the types of orientation generated in commercial forming processes, to the end that some practical application might be found. Such an application has already been made in silicon ferrite bearing preferred orientations and exhibiting these in magnetic behavior, but thus far—so far as I know—no practical application of preferred orientations has been made in automobile body steel.

Short-cut methods are much to be desired. Some years ago Tammann invented a method for the rapid determination of preferred orientations (the *Klangfiguren* method), by means of which a disk was set in vibration and a fine powder sprinkled on its surface. In absence of preferred orientations, symmetrical vibration patterns were formed; in the presence of preferred orientations, these patterns became unsymmetrical, and the degree of dissymmetry was taken as a measure of the degree of preferred orientations. With modern mechanisms for generating vibrations, particularly using piezoelectric crystals or magnetostrictive metal rods, this method could doubtless be developed much further. It is simple and should be rapid enough to satisfy industrial needs.

Tammann found some surprising facts. Mild steel bearing a preferred orientation retained at least a part of this on normalizing! Although the α - γ and the γ - α changes in iron are known to proceed by means of a well defined crystallographic mechanism, which would generate new preferred orientations to supplant the old, nevertheless considerable distortion should accompany this change and the multiplicity of orientations generated would seem so great as to erase all traces of the primary preferred orientation.

There is one important problem in this field that is quite unsolved: Why do recrystallization orientations sometimes differ entirely in type from the preferred orientations that preceded them? In copper the two types are entirely different and in iron the difference, though not radical, is marked. This problem should command the attention of investigators in this field.

* Research Physicist, New Jersey Zinc Co.

Transformation Twinning of Alpha Iron

By ALDEN B. GRENINGER,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February, 1936)

TWINNED metal crystals are usually designated as either *deformation twins* or *annealing twins*. If twins are to be classified according to the treatment the metal has undergone just prior to the observation of the twins, there are two other possible groups: (1) *solidification twins*,† when observed in the as-solidified or as-cast condition, and (2) *transformation twins*,‡ when observed in a metal which has been cooled from above an allotropic transformation temperature.

McKeehan has demonstrated that ferrite does, occasionally at least, contain twinned structures². The twins, which he studied by optical methods, were obtained during the preparation of iron single crystals by very slow cooling through A_3 . He proved that the twin relation was actually that which previous investigators had predicted; namely, twinning along three planes of the form $\{112\}$. Since McKeehan's discovery, little or no attention has been given to this transformation twinning of alpha iron, or to the possibility that it might occur at all speeds of cooling from above A_3 instead of merely during the preparation of single crystals. McKeehan's twins were evidently regarded as interesting only in proving that a body-centered cubic metal could form twinned structures—at least under certain conditions.

It is generally believed that iron seldom if ever forms annealing twins. Certainly the straight-line banding which is so abundant in annealed face-centered cubic metals is characteristically absent in iron annealed below A_3 . However, O'Neill³ has studied "twin-like" crystals in annealed alpha iron and concludes that the specimen he studied actually contained a few annealing twins. Tamura⁴ has reported "twin-like" crystals both in wrought iron and mild steel; specimens of the latter were annealed above and below A_3 and showed "twin-like" crystals after both kinds of treatments.

Manuscript received at the office of the Institute Nov. 27, 1935.

* Instructor in Metallurgy, Graduate School of Engineering, Harvard University, Cambridge, Mass.

† Verified, so far, only in slowly solidified copper. See reference 1 at end of paper.

‡ Pseudomorphic twins, if they occur in metals, would be included in this group.

The present paper embodies the results of an X-ray and optical study of transformation twins and mosaic structure in pure alpha iron.



FIG. 1.—CARBONYL IRON, PURIFIED IN HYDROGEN FOR 8 HOURS AT 1490° TO 1500° C
X 3.

Cooled through A₁ at approximately 100° C. per minute. Arrows indicate where twinning relationships have been verified. Etched with dilute HNO₃.

It represents part of a program of research into the mechanisms of crystal lattice transformations.

MATERIALS AND METHODS

Orientation relationships were determined either completely by means of back-reflection Laue X-ray photographs⁵ or by a combination of such X-ray patterns and optical goniometry. Usually, twinning planes were identified merely by means of the trace-normals plotted on the stereographic projection of the oriented twin relation. In a few cases where there was doubt as to which plane corresponded to the composition plane, the grain was sectioned and another surface prepared at 45° or 90° to the first surface; traces on two surfaces then located and identified the pole of the composition plane on the stereographic projection.

Most of the determinations were made on samples (sheets, 8 by $1\frac{1}{2}$ by $\frac{1}{16}$ in.) of purified carbonyl iron (C, 0.0022; Si, 0.0018), supplied by Mr. C. W. Briggs, of the Naval Research Laboratory.

THE TWIN RELATION

Fig. 1 shows an area on a sample of carbonyl iron purified for 8 hr. at 1490° to 1500° C. in a hydrogen atmosphere and cooled (in the water-jacketed furnace) through the A_2 point at approximately 100° C. per minute. The alpha grains are comparatively large and many of them contain banded structures which are suggestive of twins. Several of these bands were sufficiently large to permit a complete fixation of the orientation relation between bands and adjoining grain by X-ray means. The procedure in such cases was as follows: A back-reflection Laue pattern was obtained with the X-ray beam striking a band, and a subsequent pattern with the X-ray beam striking the adjoining grain, both patterns being in the same plane and with reference to the same vertical line. The orientations of both the band and the grain were then plotted stereographically.

It was found in all cases that the bands were twin bands. To date, twin relations for 12 of these orientation pairs have been determined; no other unique relationship has been found. An illustration of the twinning relation is given in Fig. 2.

Crystallized alpha iron has a pronounced macromosaic structure (Fig. 3a); that is, the grain lattice is not perfect but is composed of many mosaic lattices which show a scatter (i.e., differ from parallelism) from about 1° to about 10° .* Inasmuch as these crystals are imperfect (all the X-ray patterns of crystallized iron showed the presence of this scatter to a greater or less extent), their orientations cannot be

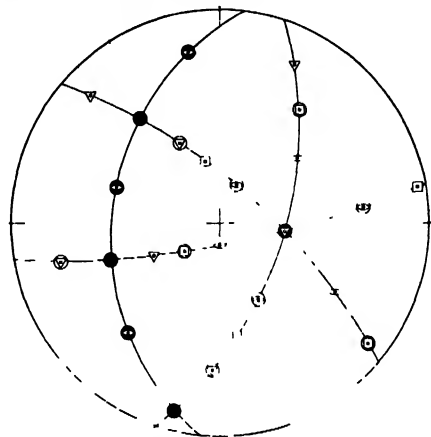


FIG. 2.—STEREOGRAPHIC PLOT OF IDEAL TWIN RELATION OF GRAIN A OF FIG. 1 AND INCLUDED DARK BANDS, SCATTERING ANGLE 3° .

$\Delta = \{111\}$ $\square = \{100\}$ $\bigcirc = \{110\}$
 $\bigcirc = \{112\}$

Plain symbols = poles of dark twin bands.

Encircled symbols = poles of grain A.
 Dark symbols = poles common to both orientations.

Great circles = the four common principal zones of the twin relation.

* This must be viewed in terms of the area that the X-ray beam strikes on the crystal, 1.5 mm. in diameter.

stated exactly, but can only be defined in terms of a mean position plus the approximate angle of scatter. It was found that the ideal twin relations always fell within the limits of the scattering angles shown on the two X-ray patterns. In no pattern has this scatter been found to be centrosymmetrical about a mean position, nor has any pattern been obtained in which the crystallographic relations of adjoining mosaics could be ascertained. Transformation twins in alpha iron must be viewed, then, with due regard to the mosaic structure of crystallized alpha iron. (As will be

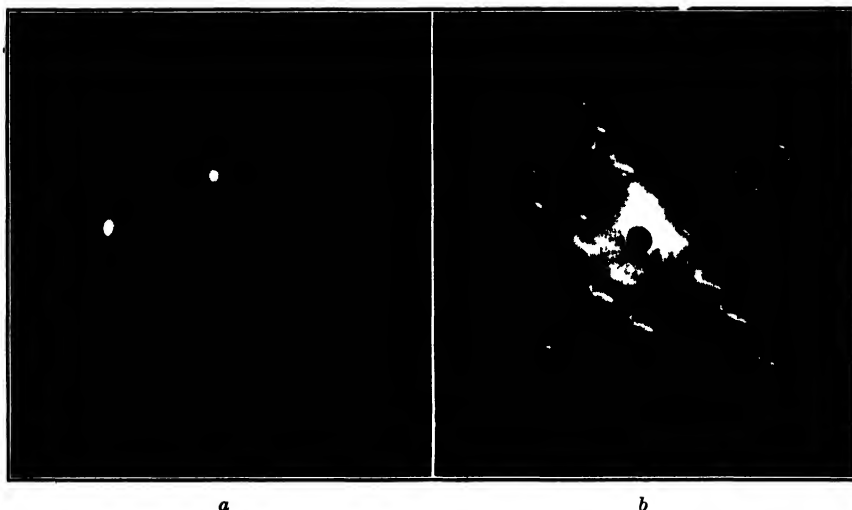


FIG. 3.—BACK-REFLECTION LAUE X-RAY PATTERNS OF ALPHA IRON.

a. After cooling through A_3 (from grain *C*, Fig. 1).

b. Deformed and recrystallized by annealing below A_3 . From specimen shown in Fig. 8.

shown later, alpha iron recrystallized by deforming 10 to 15 per cent and annealing below A_3 is completely free from macromosaic structure.)

Fig. 2 shows that so far as lattice symmetry relationships are concerned twins in alpha iron are identical to octahedral twins of the face-centered cubic metals. Thus, in any one twin relation there are: (1) one common threefold symmetry axis—and therefore a common $\{111\}$ plane; (2) three common twofold symmetry axes—and therefore three common $\{110\}$ planes; and (3) many other common planes and zone axes, among which are three common $\{112\}$ planes. There are four possible positions that a twin may assume in any one grain of alpha iron, just as there are only four twinning positions in the face-centered cubic lattice; the difference between the twins of the two lattices lies entirely in the habits assumed by the twinned grains.*

* It is because of habit characteristics (a lattice property) that twins are customarily defined by naming the twinning plane and twinning axis.

HABITS OF TRANSFORMATION TWINS IN ALPHA IRON

The habits of transformation twins in alpha iron vary not only with speeds of cooling through A_3 (see next section, Influence of Cooling Rate) but also in adjoining grains of the same sample.

Grains Containing One Set of Twin Bands.—Examples of transformation twin bands may be seen in many of the illustrations in this paper. The composition plane between the bands is always one of the three common $\{112\}$ planes of the twin relation. Even on well developed twin bands, short traces of the other two $\{112\}$ twinning planes could be found at some places along the boundary. Any one set of parallel bands corresponds to one of the four possible twin orientations; any given grain will contain a certain twin orientation in well developed bands along one $\{112\}$ plane only, even though there are three common $\{112\}$ planes for each twin orientation.

Grains Containing More than One Set of Twin Bands.—Only five grains containing two sets of well developed twin bands have been found in the samples studied thus far. (See grain *C*, Fig. 1; also Fig. 4. The two sets of bands in grain *C*, Fig. 1, both appear bright because of the convergence of the incident light.)

When two sets of bands occur in one grain, the composition plane for each band is one of the $\{112\}$ planes of the main grain, and, of course, is one of the $\{112\}$ twinning planes of the band in question. Also, there is a certain relationship between the composition plane of one band and the composition plane of the other. Their relation is such that the ideal angle between the two composition planes is $70^\circ 32'$. Of the 12 planes in the $\{112\}$ family, there are six planes each one of which is at an angle of $70^\circ 32'$ to one of the other six. Consequently, if we select arbitrarily a $\{112\}$ plane, say $(11\bar{2})$, then of the remaining 11 there is only one that is inclined at $70^\circ 32'$ to $(11\bar{2})$. It does not seem that this uniformity of composition-plane angle would be probable if the selection of the composition plane were governed by chance alone.

Grains containing three twin orientations occur rarely; no grains with three sets of well developed bands have been found so far. The fine twin bands, especially those in grains having two sets of twin bands, usually extend only a short distance through the thickness of the sheet, and hence might be regarded as having an imperfect plate shape in which one dimension is considerably longer than the other two. Large bands, found only in grains having one set, almost always extend through the entire sheet thickness.

Grains Containing No Twin Bands.—It can be stated as a general rule that, in samples such as the one illustrated in Fig. 1, any grain will: (1) contain twin bands, (2) contain smaller twin grains, or (3) have a twin relation to one or more of its neighboring grains. A grain con-

taining small twin grains will usually show the characteristics of grain *D*, Fig. 1. Neighboring twinned grains of about equal size usually have a serrated boundary line, the serrations being due to two $\{112\}$ twinning planes. However, in many twinned grains, the boundary appears at low magnification ($\times 2$ or 3) merely as an ordinary grain boundary; at higher magnifications ($\times 30$) the boundary will show an occasional saw tooth.

The Serrated End Boundary.—One of the most characteristic features of transformation twins in alpha iron is the serrated, or saw-tooth, end boundary (Figs. 1, 4, 5). A twin band is very often terminated by



FIG. 4.—TRANSFORMATION TWINS IN ALPHA IRON. $\times 20$.
Two twin orientations within one grain.
Etched with dilute HNO_3 .

either one or two of the remaining $\{112\}$ twinning planes becoming a composition plane; likewise, a twin grain may end in the same way (grain *D*, Fig. 1). The saw-tooth end boundary with straight-line serrations is generally, but definitely not always, bounded by $\{112\}$ plane traces. A few indications of $\{110\}$ traces (one of the three common $\{110\}$ planes of the twin relation) have been found. Occasionally the serrated boundaries are curved or may be very irregular at high magnification ($\times 350$).

INFLUENCE OF COOLING RATE ON HABITS OF TRANSFORMATION TWINS

Quenching from above A_3 .—Samples of carbonyl iron quenched in water from a temperature of 1100°C . showed, except for smaller grain size, all the major characteristics of habit that have been described above. The quenching operation was carried out as follows: The sample (about $1\frac{1}{2}$ by $\frac{3}{8}$ by $\frac{1}{16}$ in.) was suspended by a platinum wire in a vertical tube furnace and heated to 1100°C . in an atmosphere of purified nitrogen (time at temperature, 10 to 20 min.). The sample and wire were then allowed to fall (distance 1 ft.) into a 2-liter container filled with water (18°C). A thick layer of tissue paper on the inside bottom of the container eliminated any possibility of mechanical shock. None of the quenched specimens showed any evidence of warping.

All samples quenched in this manner showed abundant twinning (Fig. 6). No X-ray studies were made of these specimens; grains were too small for single-grain patterns, and the high degree of mosaic scatter

which could be seen by optical inspection precluded the use of double-grain or triple-grain patterns.

Slow Cooling through A_3 .—The effect of very slow cooling through the critical temperature is shown in Fig. 7. This specimen was deformed by hammering, polished, and heated to 950° C. for 3 hr. in a nitrogen atmosphere. The temperature of the furnace was then lowered so that the cooling speed on passing through A_3 was about 1° C. per min. This specimen (and all others slowly cooled through A_3) showed moderate warping. Orientations of four of the grains were determined from X-ray patterns; orientation identities were determined optically.

The specimen consists essentially of two major grains, *A* and *B*, with twin grains scattered throughout both major grains. At higher magnification ($\times 30$), occasional saw-tooth structures are visible along the various grain boundaries.

Miscellaneous.—Twins have also been observed in thick specimens of Wemco iron furnace-cooled through A_3 , and in samples of carbonyl iron annealed in vacuum and furnace-cooled through A_3 .

ANNEALING TWINS IN ALPHA IRON

It was thought that data on the relative stability of twins in alpha iron under conditions of grain growth might be obtained from a study of annealing twins. Several specimens of carbonyliron

were reduced in thickness about 10 per cent by sharp hammering (this form of cold-working develops a maximum of deformation twins). They were then annealed at different temperatures below A_3 in an atmosphere of purified and dried nitrogen gas. Fig. 8 shows one of these specimens, annealed at 900° C. for 15 hr. High-temperature annealing was necessary in order to develop grains sufficiently large for X-ray study. Specimens annealed at lower temperatures all showed essentially the same type of structure as Fig. 8, except for smaller grain sizes; that is, polyhedral grains, most of which contain small elongated grains. The latter



FIG. 5.—TRANSFORMATION TWINS IN ALPHA IRON. $\times 20$.
One twin orientation within one grain.
Etched with dilute HNO_3 .

occasionally show an imperfect banded form with serrated end boundaries.

Back-reflection Laue patterns were obtained from four of these small grains and from their four neighboring large grains. It was found that each small elongated grain was a twin of the larger grain which surrounded it. The recrystallized alpha iron showed a complete absence of macromosaic structure;* consequently the twin relations could be established accurately with double patterns. (See footnote 13 of reference 1.) Patterns were also obtained from several pairs of neighboring grains of about equal size, but in no case did such a pair of large grains have a twin relationship to one another.



FIG. 6.—CARBONYL IRON, QUENCHED IN WATER FROM 1100° C. $\times 20$. Etched with dilute HNO_3 .

Although abundant twinning was observed in these samples, the twins appear to be a minor structural constituent—certainly not at all comparable in structural prominence to the annealing twins in face-centered cubic metals.

DISCUSSION OF RESULTS

It has been shown that the two prominent structural features of pure alpha iron after cooling through A_3 are (1) transformation twins and (2) macromosaic structure. Macromosaic boundary lines undoubtedly account for some of the “veining” that has

been observed in ferrite⁶⁻⁹.

It is not possible, with the evidence available at present, to state the chronological order of formation of twins and mosaic structure. Often the twins stop (or begin?) at mosaic boundaries, but just as often they pass through boundaries; when the latter happens the twin has slightly different orientations on either side of the boundary line. The macromosaic structure of crystallized alpha iron, often visible ($\times 30$) as distinct polyhedral subdivisions or elongated subdivisions of a large alpha grain, is undoubtedly responsible for, or synonymous with, the pronounced orientation scatter of ferrite in hypoeutectoid steels.

Do the twins originate during or after the A_3 transformation? More pertinently, is the twin relation a direct result of the crystallographic uniformity of the $\gamma \rightarrow \alpha$ transformation, or does it arise after the iron

* Samples recrystallized after 2 to 3 per cent reduction in thickness (by rolling) usually have a slight macromosaic structure.

is in the alpha state? There has been one demonstration of twin formation occurring as a direct result of lattice transformation. Shoji¹⁰ has shown that when a crystal of aragonite is transformed into calcite, the result is two mean calcite orientations bearing a twin relationship to one another, with [001] of aragonite parallel to the twinning axis [111] of calcite.

An examination of the mechanisms that have been proposed for the $\gamma \rightarrow \alpha$ transformation, with reference to the possible formation of alpha twins, should be of interest. Kurdjumow and Sachs¹¹, on the basis of X-ray studies, have proposed (for the formation of martensite) the following relationship for the $\gamma \rightarrow \alpha$ transformation:

$$\begin{array}{ll} (111)\gamma & \parallel (011)\alpha \\ [10\bar{1}]\gamma & \parallel [\bar{1}\bar{1}1]\alpha \end{array}$$

Mehl and co-workers have proposed the same relationship for the transformation of pure iron¹² and hypoeutectoid steels¹³. Nishiyama¹⁴ has proposed a different relationship, as follows:

$$\begin{array}{ll} (111)\gamma & \parallel (011)\alpha \\ [\bar{2}11]\gamma & \parallel [0\bar{1}\bar{1}]\alpha \end{array}$$

Nishiyama's conclusions were based on an exhaustive X-ray study of the decomposition of single crystals of austenite (29.9 per cent Ni). Commenting on the mechanism proposed by Kurdjumow and Sachs, Nishiyama says:

The present writer considers that the displacement of atoms in the transformation resembles better that in the case of the twinning than that in the case of the translation.

He then proposes a new mechanism involving a simple shear (the twinning shear) of $19^\circ 28'$ on (111) in the direction $[\bar{2}11]$, followed by suitable expansions and contractions to complete the transformation.

All of these studies or conclusions have, of course, involved a possible error—the error inherent in attempting to assign a specific lattice relation to account for a multiple fiber structure. Thus, the pole figure of Nishiyama's relation and that of the Kurdjumow-Mehl relation are

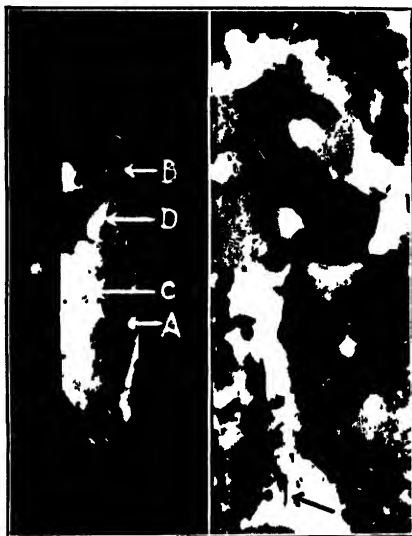


FIG. 7.

FIG. 8.

FIG. 7.—CARBONYL IRON, COOLED THROUGH A_2 AT APPROXIMATELY $1^\circ \text{C. PER MINUTE}$; ABOUT 1:1.

A and *C* are twins; *B* and *D* are twins. Small bright grains scattered throughout major grain *B* have same orientation as *D*.

FIG. 8.—CARBONYL IRON, DEFORMED BY HAMMERING AND RECRYSTALLIZED BY ANNEALING 15 HOURS AT $900^\circ \text{C.} \times 3$.

Arrows indicate where twin relation has been verified.

Both etched with dilute HNO_3 .

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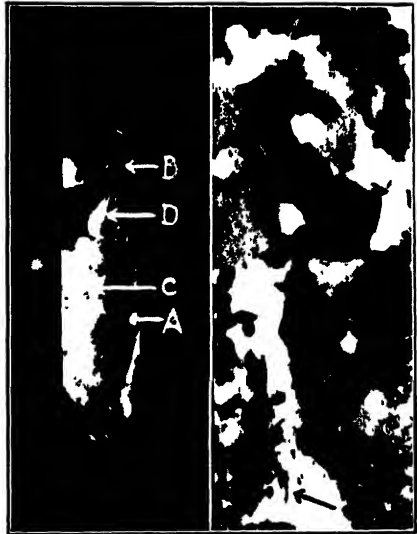


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Arrows indicate where twin relation has been verified.

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very similar; however, if the two specific relations are compared individually, the difference between them is considerable. Shoji¹⁰, working with single alpha-iron crystals and a high-temperature Laue X-ray camera, has obtained results for the $\alpha \rightarrow \gamma$ transformation which, according to him, do not agree with Kurdjumow and Sachs' mechanism. However, his study of this problem does not seem to have been very thorough. A significant result, obtained by Nishiyama for $\gamma \rightarrow \alpha \rightarrow \gamma$ and by Shoji for $\alpha \rightarrow \gamma \rightarrow \alpha$ is that the original single crystal after retransformation reverts to an imperfect single-crystal structure having a mean orientation which is the same as that of the original crystal.

The Kurdjumow-Mehl relation would produce 24 orientations of alpha from one of gamma. These 24 orientations may be segregated in groups of 12 each, and each orientation of one group bears a twin relation to one of the other group. That is, the mechanism in its ideal form would result in 12 sets of twin relations in alpha iron from each grain of gamma iron.* Likewise, an equal number of gamma twins would obtain for the reverse transformation. Nishiyama's mechanism would produce no alpha twins; but for the transformation $\alpha \rightarrow \gamma$, the result would be six sets of twin relations in gamma iron from each orientation of alpha iron.

With regard to the above statement, it is interesting to note that the saw-tooth structure, a characteristic feature of transformation twins in alpha iron, also occurs in well developed Widmanstätten structures assumed by ferrite in cast hypoeutectoid steels. An excellent example of this structure is given in Fig. 2 of the paper by Mehl, Barrett and Smith on the Widmanstätten structure of iron-carbon alloys¹². The present writer has been able to find in this figure at least eight rather sharp saw-tooth end boundaries (size, about 1 mm. in the reproduction).†

In summation, then, we might account for a number of transformation twins in alpha iron if we assume that the Kurdjumow-Mehl relationship holds for the transformation:

$$\gamma \text{ single crystal} \rightarrow \alpha \text{ single crystal,}$$

and if we assume that the transformation twins originate during the $\gamma \rightarrow \alpha$ transformation. We could not, however, account for the presence of more than one twin orientation within one alpha grain. On the other hand, we might eliminate the $\gamma \rightarrow \alpha$ transformation from consideration if we assume that the twins that have been described originate after the iron is in the alpha state.

* Evidently no attention has been given to this fact by those who have worked on segregate structures.

† An extended morphological study of such structures should yield interesting results.

SUMMARY

1. An X-ray and optical study of the orientation relationship and the habits of transformation twins in pure alpha iron has been made. In general, any one alpha grain (1) contains twin bands, (2) contains smaller twin grains, or (3) has a twin relationship to one or more of its neighboring grains.

2. The habits of transformation twins are affected by varying the speed of cooling through A_3 , mainly in the tendency of banding to disappear with very slow cooling speeds.

3. A brief study of annealing twins in alpha iron is reported; it is concluded that annealing twins are only a minor structural constituent of annealed alpha iron.

4. The mechanisms that have been proposed to explain the $\gamma \rightarrow \alpha$ transformation in iron would produce twinned structures, but do not account for the relationships between transformation twins that are reported herein.

ACKNOWLEDGMENTS

The author is indebted to Mr. C. W. Briggs, of the Naval Research Laboratory, for most of the samples of carbonyl iron used in this investigation, and to Mr. V. G. Mooradian for assistance in preparing the illustrations.

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DISCUSSION

(Francis B. Foley presiding)

F. B. FOLEY,* Philadelphia, Pa.—These alpha iron twins bring to mind the occurrence of martensite and of Widmanstätten structure in steel. We observe that transformation usually commences at crystal boundaries, but, in both these structures, transformation begins along certain crystallographic planes within the crystals and under the specific conditions that give rise to them the crystal planes act in this respect like crystal boundaries. Photomicrographs of the progress of transformation of austenite, as shown graphically by Bain's S-curve, illustrate how the transformation takes place at first in the crystal boundaries, but, as the austenite is undercooled to lower temperatures, the transformation starts along crystallographic planes giving rise to the characteristic martensitic structure. These occurrences suggest that twinning may precede the transformation and that the twin boundaries have this property in common with grain boundaries of being starting places for recrystallization. It is further noted that in 18-8, which is of course austenitic, carbides will precipitate along the twin boundaries just as they do along crystal boundaries. Many years ago, Osmond suggested that martensite results from the twinning of austenite.

G. DERGE† and R. F. MEHL,† Pittsburgh, Pa (written discussion).—The crystallographic relationships between the alpha and gamma forms of iron have been examined in numerous recent investigations, and Dr. Greninger's bibliography contains references to work in both Germany and Japan as well as in this country. Dr. Greninger's research is of exceptional interest, as he has made a fresh attack upon the problem by studying the twin relations in alpha iron and considering their origin; this is very welcome information.

The question has been put as to whether the twins originate during or after the A_2 transformation. Should not a third possibility, that the twins originated in the gamma state, be considered too? It would be possible for two gamma orientations, having the twin relation to each other, to pass through the A_2 transformation by the mechanism of Kurdjumow and Sachs and still have the twin relation in the alpha state within the 10° limit of accuracy which Dr. Greninger's macromosaic would allow. Enough data are now at hand to show that this does not occur. This possible explanation of the twins found in alpha iron was discussed by Professor Mathewson in his Institute of Metals lecture in 1928¹⁵. He showed that in all known cases the composition plane between twins in face-centered cubic metals is a $\{111\}$ plane, while Professor McKeehan found a $\{211\}$ plane to be the composition plane in his alpha iron twins, this being the only accepted example of twins in a body-centered cubic

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† Metals Research Laboratory, Carnegie Institute of Technology.

¹⁵ *Trans. A.I.M.E.* (1928) **78**, Inst. Metals Div., 7.

metal. If these twins were to have originated in the gamma state, it would therefore be necessary to show that certain twin boundary planes of $\{111\}$ type in the face-centered cubic gamma lattice had become $\{211\}$ planes in the body-centered cubic alpha lattice. Neither the crystallographic mechanism proposed by Kurdjumow and Sachs nor that of Nishiyama shows any such relationship between a $\{111\}$ gamma plane and a $\{211\}$ alpha plane. Therefore it may be concluded with some assurance that the alpha iron twins observed by Professor McKeehan and now studied more carefully by Dr. Greninger do not originate as gamma iron twins.

In the discussion of the macromosaic which he finds in alpha iron Dr. Greninger suggests that this may be closely related to the phenomena described as alpha veining. An interesting confirmation of this idea is found in meteorites, the kamacite lamellae of which show a very coarse and pronounced veining on metallographic examination, while Laue back-reflection photograms show a varying amount of scatter of the type attributed to macromosaic.

Attention has also been drawn to the finding of Nishiyama, which has since been confirmed by Wassermann, that a single crystal of iron-30 per cent nickel alloy may pass through the cycle $\gamma \rightarrow \alpha \rightarrow \gamma$ and retain the single orientation of the original gamma grain, in spite of the multiple orientations found in the alpha phase. The photograms of the alpha phase shown in these papers indicate that the gamma phase was never completely destroyed. These residual portions of gamma evidently act as nuclei which determine the orientation of the gamma formed on retransformation of the alpha, thus giving a single gamma grain instead of the multiplicity of orientations which would be expected if no such nuclei were present.

Additional work will doubtless give us a more complete knowledge of the relative importance of the twinning process described by Dr. Greninger and of the more usual type described by the relationship of Kurdjumow and Sachs, which will finally lead to a satisfactory understanding of all of these phenomena and of transformations in general.

L. W. MCKEEHAN,* New Haven, Conn.—It is naturally a great pleasure to me to see so many fine pictures of twinning in alpha iron, because the pictures I showed some years ago were then looked upon as freaks by a number of people. At that time even the expressions "twinlike structures" and "pseudo-twins" were fairly new. The new work proves that twins do occur in alpha iron, and the method used here by which one can compare the orientations is the thing I want to emphasize. Without such a technique, the determination of twin relationships on such a small scale would be very difficult.

C. S. BARRETT,† Pittsburgh, Pa.—The imperfections that are so nicely shown in this paper as a result of the transformation in purified iron are quite general; not confined to Dr. Greninger's particular samples of carbonyl iron. This fall, when we were looking for some relatively perfect iron crystals for some physical measurements, we looked over a stock of purified Wemco iron, of purified carbonyl iron, of purified mild steel and also of purified commercial iron-silicon alloys of various compositions. In every material that we knew had undergone the transformation after purification, the crystals were of the imperfect type with banded structure as shown here. Of course, we did not discover the twin relationship that has been so nicely proved here, but in every material in which the transformation had taken place these structures were present, and only in the iron-silicon alloys in which there probably was no transformation were these structures absent. Also, in every material that had been cold-worked

* Director, Sloane Physics Laboratory, Yale University.

† Physicist, Metals Research Laboratory, Carnegie Institute of Technology.

and recrystallized by annealing below the transformation, as Dr. Greninger has found, the crystals were highly perfect as far as the back-reflection photographs could show.

H. O'NEILL,* Derby, England (written discussion).—The author has kindly referred to a paper published by me in 1928, in which it was shown that certain strained and annealed alpha iron crystals contained twins lying along (112) planes. I also cited evidence suggesting that twinning in alpha iron might sometimes be associated with twinned gamma iron from which it had cooled. The author has now proved definitely that both the annealing and transformation twins do in fact exist, and the sad part about this discovery is that the presence of twinning in iron is not necessarily post mortem evidence of a previous cold-working and annealing operation. One can be sure, for instance, that twinned alpha brass has at some stage in its history been cold-worked, and it would therefore be helpful to have some method of distinguishing annealing twins in iron. It is of interest that while aluminum has been proved to give annealing twins, yet these—like their counterpart in alpha iron—are seldom straight-sided as in brass. Physicists declare that aluminum is the least “face-centered cubic” in behavior of the face-centered cubic metals: in other words it tends to act rather like a body-centered cubic material. This twinning behavior is another point of similarity.

Fig. 7 in a paper that I published in 1929¹⁸ gives good examples of “saw-tooth structures” which at the time seemed to me to be associated with the $\gamma \rightarrow \alpha$ crystallographic change. The author now shows that they are a characteristic feature of transformation twins. A few more references to alpha iron are:

17. N. P. Goss [*Trans. Amer. Soc. Steel Treat.* (1929) **16**, 405 and (1930) **18**, 1238] has shown by X-rays the existence of annealing twins.
18. Svetchnikoff [*Rev. de Mét.* (Aug. 1930)] from etch-pit evidence concludes that annealing twins exist.
19. H. O'Neill: *Trans. A.I.M.E.* (1928) Iron and Steel Div., 229, and L. B. Pfeil: *Carnegie Mem.*, Iron and Steel Inst. (1927) 153, have observed that on annealing a deformed single crystal of alpha iron the polygonal aggregate obtained gives pressure figures indicating uniform orientation. This may be explained on the basis of a twinned aggregate.

G. WASSERMANN,† Berlin, Germany (written discussion‡).—Dr. Greninger's interesting investigation of transformation twinning is a valuable enrichment of our knowledge concerning the transformation of iron at the A_3 point. The twinning orientation of the alpha crystals formed by transformation from the gamma state probably escaped earlier workers because they had in view the solution of a somewhat different question; namely, whether there was a regular orientation relationship between crystals of the different phases (alpha and beta). This question could first be explained in connection with the carbonaceous, tetragonal martensite¹¹ (twenty-four fold stratification). The somewhat different orientation relationship which Nishiyama¹⁴ determined in ferro-nickel with twelvefold stratification I also found in Ni-Fe²⁰. On the other hand, the results of Kurdjumov and Sachs were confirmed during the same investigation. The difference thus established between Fe-C (twenty-four-fold variability of orientation) and Fe-Ni (twelvefold variability of orientation) is obviously conditioned upon the action of carbon, which also causes a structural difference.

* Research Laboratory, London Midland & Scottish Railway.

¹⁸ *Jnl. Iron and Steel Inst.* (1929) **120**, 207.

† Siemens & Halske A-G Zentrallaboratorium.

‡ Translated from the German.

²⁰ G. Wassermann: *Mit. K. W. Inst. f. Eisenforsch.* (1935) **17**, 149.

The orientation relationship that Shoji¹⁰ found for unalloyed iron cannot be confirmed. It appears rather that unalloyed iron (with one exception^{12,21}, when heated above the A_1 point, always shows crystals that differ in orientation and size from those present before heating.

The martensitic transformation, which is characterized by a rigorous orientation relationship, is obviously possible only at low temperatures, where the thermal mobility of the atom is too small to consummate the process of transformation. At higher transformation temperatures, such as are present in pure iron, transformation takes place purely thermally; here it is characterized by the formation and growth of nuclei of the newly formed lattices, as in recrystallization and solidification from fusion.

Now if Sauveur²¹ and Mehl¹² have been able to find a regular orientation relationship in unalloyed iron also, this is an exception, which is not in contradiction to the above view. Through special measures, these investigators attained such rapid cooling from the gamma state that the gamma phase was undercooled to a region of slight thermal speed of transformation. The transformation temperature was thus lowered so much that the martensitic transformation mechanism leading to an exact orientation came into action.

The twinning position found of the alpha crystals that Greninger discovered now shows again that the A_1 transformation is normally a process of growth, in which the same twinning positions arise as in recrystallization. In addition, Greninger for the first time further observed that single pairs of crystals also find themselves in the orientation of the twinning transformation during the martensite transformation. Naturally, this does not indicate that an oriented transformation after the manner of martensite formation is the result with the material that Greninger investigated. In such an orientation, indeed, a great many more orientations occur, only a few of which find themselves in the twinning relation to each other.

Finally it should be remarked that the orientation of the transformation twinings to each other agrees with the orientation of the deformation twinings of alpha iron, which Mücke²² first observed. In deformation twinning the (112) plane appears as the twinning plane. The twinning plane for transformation twinning is obviously not determined yet. It is probable, though, that it will be (112) or an (111) plane here also.

A. SAUVEUR, * Cambridge, Mass.—Some years ago, we showed clearly that when iron was quenched during its allotropic transformation a decidedly Widmanstätten type of structure was obtained, very suggestive of the structure of martensite. I consider martensite as having a Widmanstätten structure on a small scale. I wonder if there is not a clear relation between the formation of twins reported by Dr. Greninger and the Widmanstätten structure.

A. B. GRENINGER (written discussion).—The suggestion that alpha twins may originate in the gamma state was made by Dr. O'Neill in England some time ago. However, for the time being at least, we can eliminate this as a possibility; gamma twins cannot pass through the $\gamma \rightarrow \alpha$ transformation as structural units, obey the Widmanstätten mechanism, and produce at the same time the habit characteristics of alpha iron transformation twins. We must, then, regard these twins as either: (1) produced during the $\gamma \rightarrow \alpha$ transformation by a mechanism which differs from the usual Widmanstätten process, or (2) produced by a lattice movement in the alpha phase (while the transformation is in progress), which must extend to the $\alpha \rightarrow \gamma$

²¹ A. Sauveur and C. H. Chou: *Trans. A.I.M.E.* (1929) **84**, 300.

²² O. Mücke: *Neues Jahrb. f. Mineral.* (1899) **2**, 55.

* Professor Emeritus, Harvard University.

interface, with the subsequent growth of the alpha phase being responsible for the habits assumed by the twins.

Dr. Wassermann has called attention to the theory, generally held by German investigators in this field, which differentiates between transformations of the Widmanstätten type (characterized by rigorous orientation relationships) and thermal transformations which proceed supposedly by random nucleation and growth. It is practically certain that the $\gamma \rightarrow \alpha$ transformation of pure iron on slow cooling through A_3 does involve nucleation and grain growth. Not only is there abundant indirect evidence for this conclusion, but this grain growth during the transformation has actually been observed and photographed with the electron microscope²³. It is by no means certain, however, that the initial nucleation is randomly oriented. Dr. Wassermann mentions his experiments in which a single crystal of alpha iron was heated above A_3 and after cooling was found to be polycrystalline with random orientation. He has evidently inferred from this that the thermal vibration of the atoms at the temperature of transformation is too great to permit an orientation relationship between the alpha nuclei and the gamma crystals from which they were formed.

The present writer cannot agree with such an interpretation of the transformation of iron. As Dr. Derge and Dr. Mehl have pointed out in their discussion, the results that both Nishiyama and Wassermann have obtained in the cyclic transformation $\gamma \rightarrow \alpha \rightarrow \gamma$ are undoubtedly due to the fact that the gamma phase of the Fe-Ni crystal was never completely transformed to alpha (shown by the X-ray pattern), but parts of it remained to act as nuclei for the reverse transformation. We might logically expect this to happen in this alloy; the sluggishness of the transformation in Fe-Ni alloys is well known. We should not, however, expect the same result from a cyclic transformation of pure iron, *unless* the single crystal of alpha iron were heated only a very few degrees above A_3 . The fact that Shoji was able to retain the orientation of the original crystal (to a limited extent) after a transformation cycle shows that the difference between the transformation of iron and iron-nickel is one of degree only. It is evident from Shoji's X-ray patterns that a large proportion of the retransformed alpha was not influenced by the small amount of alpha which must have been retained "after" the $\gamma \rightarrow \alpha$ transformation.

If we assume that the transformations α crystal $\rightarrow \gamma$ nuclei and γ crystal $\rightarrow \alpha$ nuclei tend to follow a Widmanstätten mechanism regardless of the velocity or temperature of transformation, a single crystal of alpha iron heated well above A_3 theoretically could produce on cooling 576 alpha orientations. If we consider that the pattern may be further complicated by macromosaic structure and twinning, we can well understand how an X-ray pattern of the retransformed alpha may give no clue as to the presence or absence of an oriented relationship between the alpha and gamma nuclei.

Could not all transformations, including the martensite reaction, be regarded as occurring through a process of nucleation and growth, with the orientation of the nuclei being determined within limits by the orientation of the original lattice? Variations in velocity and temperature of transformation would probably affect the scatter of orientations about the ideal position; these variables would undoubtedly determine the number of nuclei formed and affect the growth characteristics of the transformed phase.

It is hoped to discuss this problem at length in a future publication.

²³ W. G. Burgers, and J. Ploos van Amstel: Cinematographic Record of the $\alpha \rightleftharpoons \gamma$ Iron Transition as seen by the Electron Microscope. *Nature* (Nov., 1935) **136**, 721.

Choosing a Composition for Low-alloy High-strength Steel

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(New York Meeting, February, 1936)

THE new low-alloy high-strength steels are obviously here to stay. With 75 per cent higher yield strength and 50 per cent higher tensile strength than plain carbon structural steel, they permit 20 to 40 per cent weight savings and 10 per cent or more increase in pay load in the construction of railroad cars, buses, trucks, and a great variety of material-handling equipment. Their cost is low enough so that the extra cost of the new lighter construction over that with carbon steel offers an attractive self-liquidating investment; in some instances new construction with these low-alloy steels may even be as cheap as with plain carbon steel.

A considerable and rapidly growing demand for the low-alloy steels has already sprung up. The many steel compositions that have appeared on the market lately^{18,27,28,29,30} to meet this demand would seem to indicate that no single composition is uniquely fitted for the purpose. However, no doubt some compositions are more suitable than others. The purpose of this study was, therefore, to compare the effects of the various alloying elements that might be used in the low-alloy steels in order to choose the metallurgically most logical composition, paying due regard, of course, to the economic aspects involved.

PROPERTIES DESIRED IN LOW-ALLOY STEEL

A distinction between the new low-alloy steels and the common alloy steels is that the latter are generally used in the heat-treated (that is, quenched and tempered) conditions, whereas the new low-alloy steels are not only not heat-treated but are not susceptible to heat-treatment in the ordinary sense of the term. In this lies one of their chief advantages. Their properties can be obtained in the as-rolled, air-cooled, or annealed condition, just as with mild plain carbon structural steel. There is no need for heat-treating. Such steels can be readily formed hot or cold, and their properties are not appreciably changed by hot

Manuscript received at the office of the Institute Nov. 29, 1935; revised copy received March 4, 1936.

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forming. Above all, however, the steels can be readily welded, and there is neither hardening nor softening as a result of the welding heat.

These desirable characteristics are obtained by using low-carbon contents—as low as 0.1 per cent and under—so that indeed such low-alloy steel might almost be termed low-alloy iron. The fact that heat-treatment is unnecessary, the ease of working, the ductility in forming, and the ability to weld without either hardening or softening of the low-carbon low-alloy steel has overcome the suspicion with which the structural engineer usually regards alloy steel for structural uses and has given him faith in the utility of the low-alloy steels.

Another distinction between these low-alloy steels and the heat-treated alloy steels is that the tensile properties are purposely made considerably lower in the former to retain the requisite formability and weldability. The tensile properties usually associated with heat-treated medium-carbon alloy steel may be as high or higher than 100,000 lb. per sq. in. yield strength and 125,000 lb. per sq. in. tensile strength, and some of the earlier attempts to produce general purpose low-alloy structural steels aimed at these high properties. It was soon apparent, however, that these were incompatible with good formability, and the much more modest goal of 60,000 lb. per sq. in. yield strength and 75,000 lb. per sq. in. tensile strength has been generally adopted. That these properties still offer a decided advantage over plain carbon steel is attested by the growing demand for the low-alloy steels. The limits mentioned are set by the need for formability. The need for a certain amount of stiffness and rigidity in most of the contemplated structural uses for the low-alloy steels sets similar limits upon the tensile properties that can be effectively utilized—the structural members cannot be lightened unduly without loss of stiffness, unless radical changes in design are made, the value of which may be questionable.

Tensile Properties.—Since the low-alloy steels show a considerably higher increase in yield strength over plain carbon steel than in tensile strength, the full benefit of their use is obtained only when the yield strength instead of the tensile strength is made the basis of design. Most engineers are now doing this. The yield strength, of course, determines the stresses to which the structure may be subjected without permanent deformation, so that with respect to static stresses, at least, there is full justification for the use of the yield strength as the basis of design. Under repeated stresses in reversed loading, however, it is known that the endurance limit depends on the tensile strength rather than on the yield strength, the endurance ratio or ratio of endurance limit to ultimate strength being about 0.5 in carbon structural steel. Thus, with regard to repeated stresses an increase in yield strength without a corresponding increase in tensile strength would seem to be of no benefit. Fatigue tests on certain of the low-alloy steels indicate, however, that their endurance

ratio may be considerably higher than 0.5, so that even if the tensile strength is increased less than the yield strength, the increase in the endurance limit of the low-alloy steel over carbon steel may well correspond to the increase in the yield strength. Moreover, frequently structural members are not subjected to completely reversed stresses but only to partly reversed stresses. In such cases² the yield strength determines the endurance limit for these stress ranges. Haigh's³ statement that in the low-alloy steels the yield strength may be safely used as a basis for structural design both under steady loading and under alternating stresses appears to be fully justified.

Accordingly, the tensile properties desired in the low-alloy steels would be about 55,000 to 65,000 lb. per sq. in. yield strength and about 70,000 to 85,000 lb. per sq. in. tensile strength.

Ductility and Toughness.—The aim then is to attain a high yield strength without notable loss in formability. To some extent the formability is indicated by the elongation and reduction of area in a tension test and high ductility of about 25 per cent elongation in 8 in. (this will vary with the thickness of section) and about 60 per cent reduction of area is desired. However, just as the ductility in the tension test does not fully indicate the deep-drawing properties of sheet steel, so it does not fully indicate the formability. In deep-drawing sheet the tensile test is supplemented by an Olsen or other form of cupping test. In these low-alloy steels the tension test should be supplemented by a bend test. Recent work by Gough⁴ would indicate that a bend test is about as good a measure of formability as we have.

The desired bend properties, of course, will vary with the gage of the sheet or plate, but it may be stated that the thinner gages should show a full flat bend in the longitudinal and transverse directions, and the thicker sections should show correspondingly good bend properties.

The notched-bar impact resistance offers a good measure of the toughness, although the exact value is difficult to determine on thin sheet because the standard impact specimen is considerably thicker. However, comparative values in notched-bar impact tests of even thin sheet may give a good indication of the toughness and may be of particular value when the notch is placed in or immediately adjacent to a weld. A notched-bar impact value corresponding to an impact resistance of about 50 ft-lb. on a full-sized Charpy specimen, with a silky or other ductile type of fracture, should be obtained.

Workability, Cold and Hot.—Cold formability has already been discussed. There is no difficulty in hot-forming any of the structural alloy steels. What must be obviated is hardening on air-cooling from the hot-forming temperature, and this can be done, as has been stated, when the carbon and the other elements that favor air-hardening are kept low. Steels that will not harden appreciably on air-cooling will show only

slight variations in tensile properties in sections of different thicknesses, in the hot-rolled condition, after air-cooling from the finishing temperature in rolling.

Weldability.—Welding has become such an important process in modern construction that this is an all-important consideration. As has been indicated, the main thing is to obviate hardening on air-cooling from the welding heat. Welding technique has been improved so greatly recently that practically any steel of the low-alloy type can be welded to give a sound weld. With some of the alloying elements it may perhaps be more difficult to obtain sound welds than with others, but altogether too little is known about the effect of the different alloying elements in this respect. With some of the additions grain growth and consequent embrittlement due to the welding heat are perhaps more apt to occur than with others. Notched-bar impact tests in and adjacent to the weld at atmospheric and subatmospheric temperatures may be used to detect such embrittlement.

Corrosion Resistance.—The recent great interest in the low-alloy steels is in large measure due to the discovery that they may have appreciably greater atmospheric corrosion resistance than plain carbon steel. Thus, lighter weight construction with such low-alloy steels should resist weathering at least as well as heavier construction with plain carbon steel. Of course, in many services wear is the limiting factor, and enhanced corrosion resistance is not essential. Atmospheric corrosion resistance is also not so important in painted and in galvanized structures as in bare structures. On the whole, a several-fold increase in atmospheric corrosion resistance such as is obtainable with some of the low-alloy steels is a distinct asset.

EFFECT OF THE DIFFERENT ELEMENTS

The mechanical properties, weldability, and corrosion resistance must, therefore, be considered in choosing a low-alloy steel composition.

Mechanical Properties.—Before presenting the comparative data on the different alloy compositions that were tested in this study, a “merit factor,” which was helpful in discriminating between them in regard to the mechanical properties, should be discussed.

The primary aim in the low-alloy steels is to increase the yield strength to well above that in carbon steel without at the same time reducing the formability unduly. Now the formability, particularly in sheet or plate, can best be defined in terms of the bending properties, as indicated by a bend or repeated bend test. Rather definite indications were obtained during this work that the hardness or tensile strength rather than the yield strength limits the bend properties in these types of steels. That is, a steel with a higher yield strength but lower tensile strength has better

bend properties than a steel with a lower yield point but higher tensile strength. A simple way to express this is to state that for a certain yield strength better formability will be obtained with steels of higher elastic ratio $\left(\frac{\text{yield strength}}{\text{tensile strength}}\right)$ than with steels of lower elastic ratio. This is illustrated in Table 1. Steel 1, with a higher yield strength but lower tensile strength had better bend properties than steel 2, with lower yield strength but higher tensile strength.

TABLE 1.—*Elastic Ratio as a Criterion of Formability*

Steel No.	Compositions ^a , Per Cent								Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb per Sq. In.	Elonga- tion, Per Cent in 2 In	Repeated Bends ^b	Elastic Ratio
	C	Mn	P	S	Si	Cu	Ni	Cr					
1	0.08	0.52	0.017	0.029	0.182	1.06	0.60		50,500	65,500	33	5	0.76
2	0.08	0.45	0.017	0.028	0.174	1.05	0.48	1.25	42,500	75,500	29	3	0.56

^a The specimens were rolled into 0.125-in. gage sheets from 15-lb. experimental induction-furnace melts and tested in the normalized condition, air-cooled from 1650° F.

^b In the repeated-bend tests the specimens were bent repeatedly around a $\frac{1}{8}$ -in. radius, first through 90° in one direction, then through 180° in the reverse direction, and back again until the specimen broke. The reported figures are for the number of reversals through 180°.

In the many cases where accurate bend tests are difficult to make, the elastic ratio should constitute a very helpful criterion of formability.

TABLE 2.—*Elastic Ratio as a Merit Factor^a*

Heat-treatment	Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In	Reduction of Area, Per Cent	Isod Impact, Ft.-lb.	Elastic Ratio
Annealed 1650° F., water quenched 1550° F., tempered 1250 to 1275° F	63,000	92,000	26	56.5	56	0.68
Annealed 1650° F., air-cooled 1550° F., tempered 1250 to 1275° F	55,000	87,500	27.5	48	33	0.63
Annealed 1650° F., furnace-cooled	52,000	86,000	26.5	45.5	16.5	0.60

^a These unpublished data were obtained by the Committee on Impact Testing of Steel Castings of the American Foundrymen's Association on a nickel-manganese cast steel of the following composition: C, 0.34 per cent; Mn, 1.18; Si, 0.32; S, 0.036; P, 0.031; Ni, 0.76.

That it may in general be used also as a "merit factor" is indicated by Tables 2 and 3. For the steels heat-treated to the same tensile strength, there was a decided difference in reduction of area and impact resistance;

the steels with the higher reduction of area and impact resistance also had a higher elastic ratio.

TABLE 3.—*Elastic Ratio as a Merit Factor*

Material ^a	Yield Strength, Lb. per Sq. In	Tensile Strength, Lb. per Sq. In	Elongation, Per Cent in 2 In	Reduction of Area, Per Cent	Elastic Ratio
Normalized 0.6 per cent C steel.	58,000	114,000	18	34.4	0.51
Quenched and tempered Ni-Cr steel	86,000	112,000	18	60.0	0.77

^a Data obtained from L. W. Schuster⁵.

Having indicated that the elastic ratio may be a helpful criterion in choosing a low-alloy steel composition, we may consider the manner in which the various elements tend to strengthen iron. The effect of carbon on the tensile properties of hot-worked iron-carbon alloys is shown in Fig. 1. Keeping in mind the aim of raising the yield strength, it will be observed that carbon does this, of course, but that as the yield strength increases, the tensile strength increases at a much faster rate. Thus, at the carbon content at which a yield strength of about 60,000 lb. per sq. in. would be obtained, the tensile strength is so high that the steel will not be formable. This clearly indicates why plain iron-carbon alloys cannot be used in making high-strength formable steels. In contrast to the effect of carbon, Fig. 2 shows the effect of copper. As copper is added to iron, the yield strength increases, and so, of course, does the tensile strength, but at a rate no faster, in fact slightly slower, than the yield strength. Instead of the yield-strength and tensile-strength lines spreading out as they do with increasing carbon, the lines even tend to converge slightly. Thus when a yield strength of 60,000 lb. per sq. in. is obtained with iron-copper alloys, the tensile strength is still low enough to give good formability.

The other alloys can also be roughly grouped into (A) those in which the yield-strength and tensile-strength lines spread out as the alloy is added, and (B) those in which these lines either remain parallel or converge slightly, as follows:

A. Spreading lines

Carbon
Manganese
Chromium
Silicon
Molybdenum

B. Parallel or converging lines

Copper
Phosphorus
Nickel

Figs. 1 to 8 indicate the effects of the above alloys on the yield strength and tensile strength after air-cooling. The curves were drawn from the available data in the literature, which in most cases were somewhat inadequate, but it is believed that the curves are probably qualitatively

correct. The lines for the effects of chromium, silicon, molybdenum, copper, phosphorus, and nickel were obtained on low-carbon alloys; those for manganese were obtained on a 0.55 per cent carbon steel as well as for low-carbon alloys. In group A, with the spreading lines, carbon

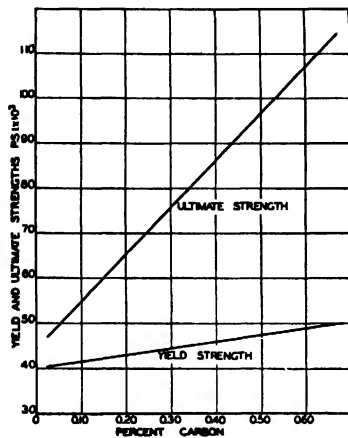


FIG. 1.

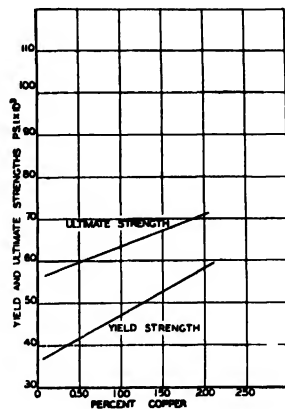


FIG. 2.

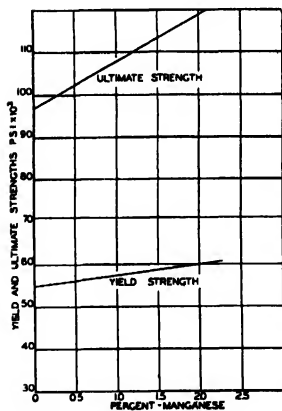


FIG. 3.

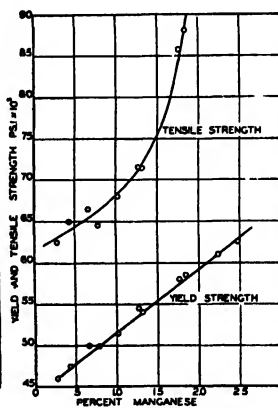


FIG. 3a.

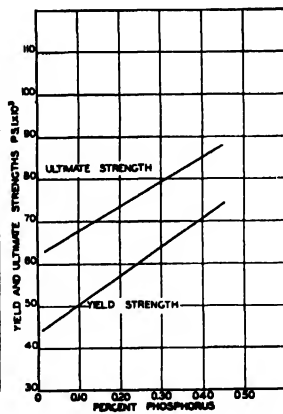


FIG. 4.

FIGS. 1-4.—EFFECT OF ADDING VARIOUS ELEMENTS ON THE YIELD STRENGTH AND TENSILE STRENGTH OF IRON.

Fig. 1.—Fe-C (*Nead*⁶). Spreading lines.

Fig. 2.—Fe-Cu (*Brevit*⁷). Parallel or converging lines.

Fig. 3.—Fe-Mn (*Bain*⁸) for 0.55 per cent C steel. Spreading lines.

Fig. 3a.—Fe-Mn (*Lang*¹¹) for low-carbon steel. Spreading lines.

Fig. 4.—Fe-P (*d'Amico*⁹). Parallel or converging lines.

shows by far the most rapid spread; manganese is next, followed by chromium and silicon, and molybdenum is last with very slight spreading. In group B, with the parallel or converging lines, copper converges the lines most rapidly; phosphorus is next, and nickel is last with virtually parallel lines. These relations apply for the ranges of alloy contents that

ordinarily would be used in the low-alloy steels, although they may not apply for much higher contents of some of the elements.

Whether or not the effects indicated by Figs. 1 to 8 are additive, or to what extent they may be so, is uncertain, and the relative elastic ratios of complex low-alloy steels cannot, therefore, be predicted.

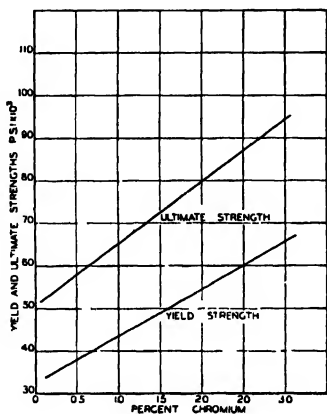


FIG. 5.

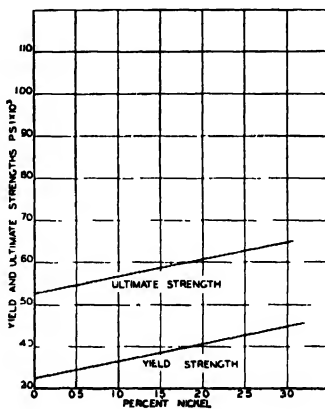


FIG. 6.

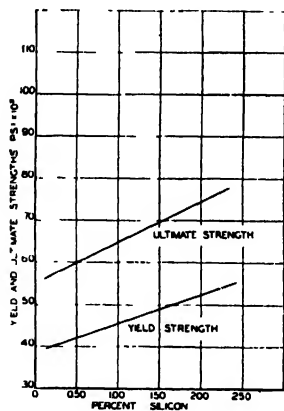


FIG. 7.

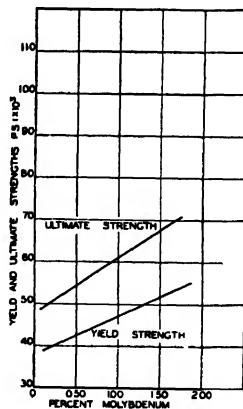


FIG. 8.

FIGS. 5-8.—EFFECT OF ADDING VARIOUS ALLOYING ELEMENTS ON THE YIELD STRENGTH AND TENSILE STRENGTH OF IRON.

Fig. 5.—Fe-Cr (*Wright and Mumma*¹⁰). Spreading lines.

Fig. 6.—Fe-Ni (*International Nickel Co.*¹¹). Parallel or converging lines.

Fig. 7.—Fe-Si (*Pagham*¹²). Spreading lines.

Fig. 8.—Fe-Mo (*Hadfield*¹³). Spreading lines.

Data in the literature on the tensile properties of such steels appear to give no clear-cut indications that steels with copper, phosphorus and nickel have higher elastic ratios than those with manganese, chromium, silicon and molybdenum. Of course, the condition of the steel has a decided effect on the elastic ratio. Fine-grained steels and "cold-worked" steels (as in lighter gage sheet finished near or below the critical

temperature in rolling) generally have a higher elastic ratio than coarse-grained or normalized or annealed steels; age-hardened steels, as in the age-hardening copper steels, have a very high elastic ratio. This is probably the reason why it is so difficult to draw definite conclusions from published data.

On the other hand, fairly definite indications were obtained from experimental melts made in this study that, likewise in complex analyses approximating commercial compositions, the effects of the elements on the elastic ratio are qualitatively as indicated by Figs. 1 to 8. Tensile-test data on an experimental series of compositions made in 50-lb. induction-furnace melts and rolled into 0.062-in. thick sheets are given in Table 4. The tests were made of the sheets in the normalized condition. It is not intended to imply that the same properties would be obtained on large commercial heats of steel rolled according to regular practice, but it is believed that the values are indicative in a general way of the effect of the alloying elements concerned.

TABLE 4.—*Effect of Carbon on Tensile Properties of Steels Made from Experimental 50-lb. Induction-furnace Ingots*
NORMALIZED 0.062-IN. GAGE SHEETS

Steel No	Composition, Per Cent								Yield Strength, Lb per Sq. In	Ultimate Strength, Lb per Sq. In	Elongation, Per Cent in 2 In	Elastic Ratio
	C	Mn	P	S	Si	Cu	Cr	Mo				
1	0 08	0 28	0 144	0 036	0 63	0 44			45,000	60,000	29	0 75
2	0 13	0 73	0 226	0 036	0 20	1 43			57,750	84,000	24	0 69
3	0 14	0 68	0 016	0 032	0 23	1 39			52,000	74,500	24	0 70
4	0 14	0 53	0 017	0 035	0 19	1 34	0 48		51,500	72,500	28	0 71
5	0 15	0 70	0 222	0 029	0 19		1 09		44,000	78,500	20	0 56
6	0 27	0 97	0 017	0 035	0 30				49,500	86,000	20	0 58
7	0 28	1 36	0 032	0 025	0 69		0 41		57,000	105,000	14	0 54
8	0 29	0 95	0 018	0 038	0 33				48,000	86,500	22	0 56
9	0 31	1 56	0 017	0 039	0 23			0 26	56,000	100,750	17	0 55
10	0 32	0 81	0 018	0 037	0 18				47,500	83,750	25	0 56
11	0 32	0 76	0 013	0 028	0 30				42,500	76,500	26	0 56

The steels in Table 4 have been divided into two groups according to the carbon contents. The average elastic ratio for the lower carbon content group is considerably higher than for the higher carbon content group. The elastic ratio of steel No. 5 is definitely lower than for the others in its group; apparently the lowering of the yield strength and elastic ratio was caused by the presence of the chromium. A similar effect of chromium is indicated by the data previously given in Table 1.

That low-alloy compositions higher in manganese and silicon tend to give lower elastic ratios than steels with similar base compositions but lower manganese and silicon contents is indicated in Table 5. The steels have been divided into two groups, 1 to 4, with relatively lower manganese

and silicon contents, and 5 to 9, with higher manganese and silicon contents. The latter group has a lower average yield strength and elastic ratio.

TABLE 5.—*Effect of Manganese and Silicon on Tensile Properties of Steels Made from Experimental 15-lb. Induction-furnace Ingots*

NORMALIZED $\frac{3}{8}$ -IN. THICK SHEETS

Steel No.	Composition, Per Cent						Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Elastic Ratio
	C	Mn	Si	Cu	Ni	Cr				
1	0.17	0.68	0.53	0.90		0.60	54,000	80,500	33	0.67
2	0.15	0.75	0.50	0.80	0.45	0.60	61,500	83,500	32	0.74
3	0.15	0.75	0.50	0.75	0.30	0.50	53,000	81,000	32	0.66
4	0.15	0.75	0.50	0.90		0.60	65,000	98,500	28	0.66
5	0.13	1.11	0.77	0.50		0.50	41,500	80,000	36	0.52
6	0.12	1.00	0.75	0.50		0.50	50,000	80,000	35	0.62
7	0.10	1.50	1.00				47,500	90,000	35	0.53
8	0.14	1.29	1.06	0.50			56,000	85,000	33	0.66
9	0.13	2.00	0.50	0.50		0.50	48,000	93,000	32	0.52

The relative effects of copper and of chromium on the elastic ratio are well illustrated in Table 6, of two open-hearth steels poured into full-sized ingots and rolled according to regular practice on a hot strip mill, one with high copper and low chromium and the other with low copper and high chromium. The second steel had definitely lower yield strengths and elastic ratios in the normalized, blue-annealed, box-annealed, and normalized and box-annealed conditions. In the as-rolled condition the high-chromium low-copper steel had the same elastic ratio as the low-chromium high-copper steel. This is, no doubt, because of the raising of the yield strength by the "cold-work" effect in hot-rolling the relatively thin sheet. However, a high yield strength obtained by this means will not persist after heating for hot-forming or in welding. The decidedly lower yield strength and elastic ratio of the high-chromium low-copper steel in the box-annealed and box-annealed and normalized condition is of especial interest. These data would indicate that the higher chromium steels are more likely to suffer a sharp drop in yield strength and elastic ratio on annealing, which treatment is, of course, frequently practiced for the softening of thin gage sheets after hot-rolling.

The reputation of the nickel-chromium medium-alloy steels is so high that it is rather surprising to find that chromium has the same effect in lowering the elastic ratio in a low-carbon, 2 per cent nickel, 1 per cent copper steel, as in steels without or with very low nickel (Table 7). These chromium-nickel-copper and nickel-copper steels have been divided

into two groups with low phosphorus and with high phosphorus content. The decided effect of chromium in lowering the elastic ratio is apparent.

In these steels phosphorus had no effect in raising the elastic ratio, although it did tend to raise the yield strength somewhat. The effect of phosphorus in a 1 per cent copper, 0.6 per cent nickel steel is shown in

TABLE 6.—*Tensile Properties of Commercial 0.125-in. Gage Sheets Comparing a High-copper Low-chromium Steel with a Low-copper High-chromium Steel*

Steel	Composition, Per Cent						
	C	Mn	P	S	S ₁	Cu	Cr
High-copper low-chromium. . .	0 14	0 56	0 19	0 24	0 24	1 22	0 42
Low-copper high-chromium.	0 17	0 43	0 17	0 29	0 52	0 22	1 27

Alloy Type	Condition	Yield Strength, Lb per Sq In	Tensile Strength, Lb. per Sq In	Per Cent Elongation in 8 In	Elastic Ratio
High Cu, low Cr Low Cu, high Cr	As rolled ^a	62,750	79,250	24	0 79
		66,250	84,250	22	0 79
High Cu, low Cr Low Cu, high Cr	Normalized ^b	59,500	74,750	24	0 80
		56,500	77,500	23	0 73
High Cu, low Cr Low Cu, high Cr	Blue-annealed ^c	60,250	76,000	21	0 79
		56,250	79,000	23	0 71
High Cu, low Cr Low Cu, high Cr	Box-annealed ^d	69,750	84,250	15	0 83
		52,250	77,500	23	0 67
High Cu, low Cr Low Cu, high Cr	Normalized and box-annealed ^e	59,750	74,250	20	0 80
		47,500	74,500	26	0 64

^a Finishing temperature about 1700° F. ^c Air-cooled from 1525° F.

^b Air-cooled from 1800° F.

^d Box-annealed at 1250° F.

^e Normalized at 1800° F.; box-annealed at 1250° F.

Table 8. The addition of 0.2 per cent phosphorus raised the yield strength decidedly without unduly increasing the tensile strength, so that the elastic ratio also increased somewhat.

Weldability.—This may be defined in terms of: (1) soundness of the weld or its freedom from porosity and refractory inclusions which may cause incomplete welding, and (2) the absence of undue hardening and embrittlement of the weld and base metal and of high residual stresses. The latter effects will be practically harmless in low-carbon steels with only small amounts of hardening elements. With regard to porosity

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and incomplete welding, virtually no systematic data on the effects of the various elements are available. In general, lower carbon steels weld better because there is less gas evolution arising from the reaction of carbon with iron oxide; this may be largely overcome, however, by the addition of manganese and silicon.

TABLE 7.—*Effect of Chromium on Tensile Properties of 2 Per Cent Nickel, 1 Per Cent Copper Steel*

NORMALIZED 0.125-IN. GAGE SHEETS FROM 15-LB. INDUCTION-FURNACE MELTS

Steel No.	Composition, Per Cent								Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Elastic Ratio
	Cr	C	Mn	S	Si	Cu	Ni	P				
1		0.07	0.45	0.029	0.192	0.98	1.97	0.021	58,000	69,500	30	0.83
2	0.70	0.08	0.49	0.030	0.205	0.94	1.97	0.018	57,500	88,000	25	0.65
3		0.08	0.42	0.025	0.140	0.96	1.94	0.118	60,000	76,000	29	0.79
4	0.71	0.07	0.36	0.028	0.210	0.89	2.15	0.118	58,500	89,000	25	0.66

TABLE 8.—*Effect of Phosphorus on Tensile Properties of Low-alloy Steel*

NORMALIZED 0.125-IN. GAGE SHEETS FROM 15-LB. INDUCTION-FURNACE MELTS

Composition, Per Cent							Yield Strength, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Elastic Ratio
P	C	Mn	S	Si	Cu	Ni				
0.017	0.08	0.52	0.029	0.18	1.06	0.60	50,500	65,500	33	0.77
0.191	0.08	0.45	0.028	0.18	0.97	0.59	59,000	74,500	32	0.79
0.195	0.07	0.31	0.028	0.10	0.99	0.58	59,500	74,000	31	0.80

Hatfield¹⁵ states that manganese is regarded as beneficial, but that opinions differ regarding the effect of silicon. It may be significant that manufacturers of welding rod tend to limit the silicon content. Lawrence¹⁸ states that in plates for fusion welding the silicon content is generally limited to 0.25 per cent. On the other hand, Leitner¹⁶ found that a higher silicon content of 0.6 per cent and above gave less porous welds. Kinzel¹⁷ states that harmful effects of excess silicon or aluminum in the steel can be overcome by regulating the coating of the electrode to flux the refractory oxides, which would otherwise form.

Hatfield¹⁵ states that no harmful oxidizing effects result from the presence of chromium if suitable flux coatings are used, the main objection to chromium being its tendency to cause undue hardening unless the carbon is kept very low.

Molybdenum also has no harmful oxidizing effects, and high percentages of ferromolybdenum are used in the coatings of welding rods for welding low-alloy high-strength steels. Like chromium, it may cause undue hardening, however, unless the carbon is low.

That copper is not regarded as harmful is indicated by its common use as a covering for welding rods for gas welding. Gregg and Daniloff¹⁹ concluded that the weldability of steel in arc or gas welding is not impaired by about 0.75 per cent or possibly more of copper, and that the presence of copper in welding rod tends to improve the ductility of the welds.

The reputed excellent welding quality of Bessemer steel indicates that phosphorus has no bad effect on weldability in so far as the formation of a sound weld is concerned. Indeed, Powell²⁰ found that in the plastic welding of hard edge tools to a soft steel backing the presence of about 0.10 per cent phosphorus was of benefit in reducing the number of defective welds. Where grain growth results on prolonged high-temperature heating during welding, the presence of phosphorus may cause embrittlement. However, this may be readily avoided with ordinary welding technique in low-alloy steels of the proper composition containing about 0.15 per cent phosphorus, as indicated by the impact test results of welded sheets described later in this paper.

Hatfield¹⁵ states that there has been a widely held view that nickel was detrimental to weldability, but that accumulated experience indicates this view to be erroneous, and that nickel steel can be successfully welded with comparative ease. Of course, as in all such cases the composition must be controlled so that undue hardening does not occur.

Corrosion Resistance.—It is a fortunate fact that the same elements, copper and nickel, that are most effective in raising the yield strength without unduly reducing the formability, have recently been proved very effective in increasing the atmospheric corrosion resistance of low-alloy steels. Not so long ago most metallurgists were highly skeptical of attempts to raise the corrosion resistance of carbon steel by additions of an alloying element. The feeling was that after all iron was iron and that it would rust away unless highly alloyed, as in stainless steel. This is still the situation for submerged and underground corrosion, where the relatively small alloy additions used in the low-cost low-alloy steels have so far appeared to be without avail in reducing the rate of corrosion. However, in the atmosphere, as in ordinary weathering, the presence of copper and of phosphorus has been shown by the tests of the American Society for Testing Materials^{21,22} and a host of other evidence¹⁹ to raise the corrosion resistance to two and three times above that of plain carbon steel. Recent data by Daeves²² indicate that over 0.06 per cent phosphorus materially aids the atmospheric corrosion resistance of copper-bearing steel. Phosphorus was found to aid in the formation of a smooth adherent rust coating with no rough scars or granules that can readily flake off.

Nickel probably aids corrosion resistance²³, although no published data on atmospheric corrosion tests are available.

Whetzel²⁷ states that carbon, manganese and silicon do not tend to increase the atmospheric corrosion resistance of low-alloy steels.

The effect of chromium in the amounts in question is very uncertain. In ordinary iron, up to about 1 per cent of chromium appears to have little or no effect on the atmospheric corrosion resistance. Whetzel²⁷ states that no claims for increased corrosion resistance for the German copper-chromium steels were made by the manufacturers. Speller²² states, however, that the addition of 1 per cent chromium to a copper steel will about double its atmospheric corrosion resistance.

Eisenkolb²⁴ found that the superior atmospheric corrosion resistance of copper steels appeared to be enhanced by small additions of molybdenum.

SELECTED COMPOSITION

After the foregoing, the basis for choosing the selected composition can be summarized as follows:

Carbon.—Less than 0.10 per cent.

Manganese.—Since this tends to lower the elastic ratio and increase the hardenability and does not improve the corrosion resistance, it appears preferable to hold the manganese content at about 0.50 per cent, which is ample to insure good rolling and welding properties.

Silicon.—This element also tends to lower the elastic ratio and has no beneficial effect on the corrosion resistance. Lorig and Krause²⁵ state that silicon tends to accentuate embrittlement by phosphorus. It appeared preferable, therefore, to maintain the silicon content at about 0.15 per cent, which is ample for obtaining a killed steel, and is also low enough to relieve any doubts as to the possible harmful effect of a high-silicon content on the weldability.

Chromium.—This element tends to lower the elastic ratio and to increase the hardenability. It appeared advisable, therefore, to omit chromium from the selected composition. However, if it should be found that chromium materially improves the corrosion resistance, it may be desirable to use some chromium in these low-alloy steels.

Copper.—This element is the most effective one in raising the elastic ratio, and about 1 per cent copper in the selected composition appears sufficient to give a yield strength of 60,000 lb. per sq. in. This percentage of copper does not harm the weldability and materially improves the corrosion resistance.

Nickel.—This element is not so effective as copper in raising the elastic ratio, as has been observed by Gibson¹⁴, nevertheless it belongs with the group of elements that does not raise the tensile strength unduly as the yield strength increases. Moreover, the presence of about half as much nickel as copper is essential in overcoming the tendency for checking in the rolling of copper-bearing steels. Therefore about 0.5 per

cent nickel is used in the selected composition, and this nickel content may also have a beneficial effect on the corrosion resistance. Whether a still larger addition of nickel would further enhance the corrosion resistance to a point justifying its use is questionable and remains to be demonstrated.

Phosphorus.—This element tends to raise the yield strength sharply without lowering the elastic ratio. It distinctly improves the atmospheric corrosion resistance. Lorig and Krause²⁵ have shown that over 0.20 per cent phosphorus in a properly made fine-grained steel does not cause embrittlement. Phosphorus does not injure and probably benefits the weldability, if the composition is properly adjusted to avoid embrittlement by the welding heat. Therefore about 0.12 per cent phosphorus was used in the selected composition.

Selected composition of the copper-nickel-phosphorus steel is as follows: C. 0.10 per cent max.; Mn, 0.50; Si, 0.15; Cu, 1.00; Ni, 0.5; P, 0.12.

TEST RESULTS ON SELECTED COMPOSITION

There follow data on the tensile, bend and impact properties of the selected composition and data on these properties after arc and gas welding. For comparison purposes similar tests were made of a copper-

TABLE 9.—*Compositions of the Low-alloy Commercial Sheet Steels Tested*^a

Designation	Type Composition	Analysis, Per Cent							
		C	Mn	Si	P	S	Cu	Ni	Cr
A	Selected, composition Cu-Ni-P	0 080	0 480	0 130	0 120	0 024	1 050	0 47	
B	Selected composition Cu-Ni-P + 0 35 Cr	0 080	0 480	0 130	0 118	0 025	1 060	0 50	0 35
C	Cu-Ni-Cr	0 070	0 420	0 224	0 010	0 023	0 800	0 450	0 69
D	Copper-bearing plain carbon	0 080	0 38		0 008	0 026	0 25		
E	Plain carbon	0 080	0 38		0 007	0 026			

^a These were commercial sheet made and rolled according to regular commercial practice.

nickel-chrome steel, a plain low-carbon steel, and a low-carbon copper-bearing steel. A comprehensive program of atmospheric corrosion tests of these steels is now under way.

Tensile, Bend and Impact Properties.—The compositions of the steels tested are given in Table 9. Data on tensile, bend and impact tests of the sheet material used are given in Table 10. All the values are averages of two tests. The manner of making the repeated bend tests was given in a footnote to Table 1. The flat bend tests were made by starting a

TABLE 10.—Results of Tensile, Bend and Impact Tests of the Low-alloy Commercial Sheet Steel Tested

Material	Gage, In	Yield Strength, Lb per Sq In	Tensile Strength, Lb per Sq In	Elastic Ratio	Elonga- tion, Per Cent in 8 In	Red of Area, Per Cent	Longitudinal Bend Tests		Impact Values, Ft.-lb.					Rockwell B Hardness
							Re- peated	Flat	Testing Temperature					
									+23° C	0° C	-25° C	-40° C		
A as rolled	0 062	73,000	80,000	0 915	23		8 0	OK	27 9	29 3	28 4	29 9	89 3	
A normalized ^a	0 062	61,500	75,000	0 82	21		10 5	OK	29 3	30 5	32 3	28 7	84 1	
B as rolled	0 062	72,000	81,500	0 88	22		10 5	OK	28 1	29 7	29 7	27 9	87 9	
B normalized	0 062	62,500	77,250	0 81	21		11 0	OK	31 2	30 9	31 5	29 7	85 9	
C as rolled	0 062	65,000	75,000	0 865	24		10 5	OK	33 8	33 9	36 0	33 0	84 1	
C normalized	0 062	52,000	68,000	0 765	25		14 0	OK	33 9	36 8	36 8	34 8	78 4	
D as rolled	0 062	42,400	51,250	0 83	31		16 0	OK	29 8	31 3	29 5	30 4	59 5	
D normalized	0 062	36,750	50,000	0 735	26		21 0	OK	28 9	31 6	31 0	29 8	55 8	
E as rolled	0 062	41,000	52,000	0 79	14		15 5	OK	27 1	29 3	29 0	29 3	64 7	
E normalized	0 062	34,750	49,000	0 705	26		16 5	OK	31 1	30 2	30 6	29 3	54 7	
A as rolled	0 125	69,100	77,900	0 885	22	68	4 5	OK	41 7	44 2	42 2	35 8	87 9	
A normalized	0 125	62,500	74,500	0 84	25	68	5 0	OK	46 0	47 0	46 3	43 6	82 2	
B as rolled	0 125	69,900	80,300	0 87	23	65	4 0	OK	41 7	45 8	47 0	38 4	84 3	
B normalized	0 125	62,750	77,750	0 81	23	71	5 0	OK	44 1	45 7	40 7	36 2	84 0	
A as rolled	0 250	57,200	72,300	0 79	28	57		OK	45 0	43 8	40 1	46 5	82 3	
A normalized	0 250	60,250	72,000	0 835	25	76		OK	62 5	57 9	54 0	33 2	82 8	
B as rolled	0 250	53,300	72,000	0 77	30	58		OK	52 6	49 5	44 4	45 7	82 7	
B normalized	0 250	55,250	71,750	0 77	26	75		OK	56 9	61 0	57 0	45 5	83.7	

^a The sheets as received were heated to 1650° F. and air-cooled

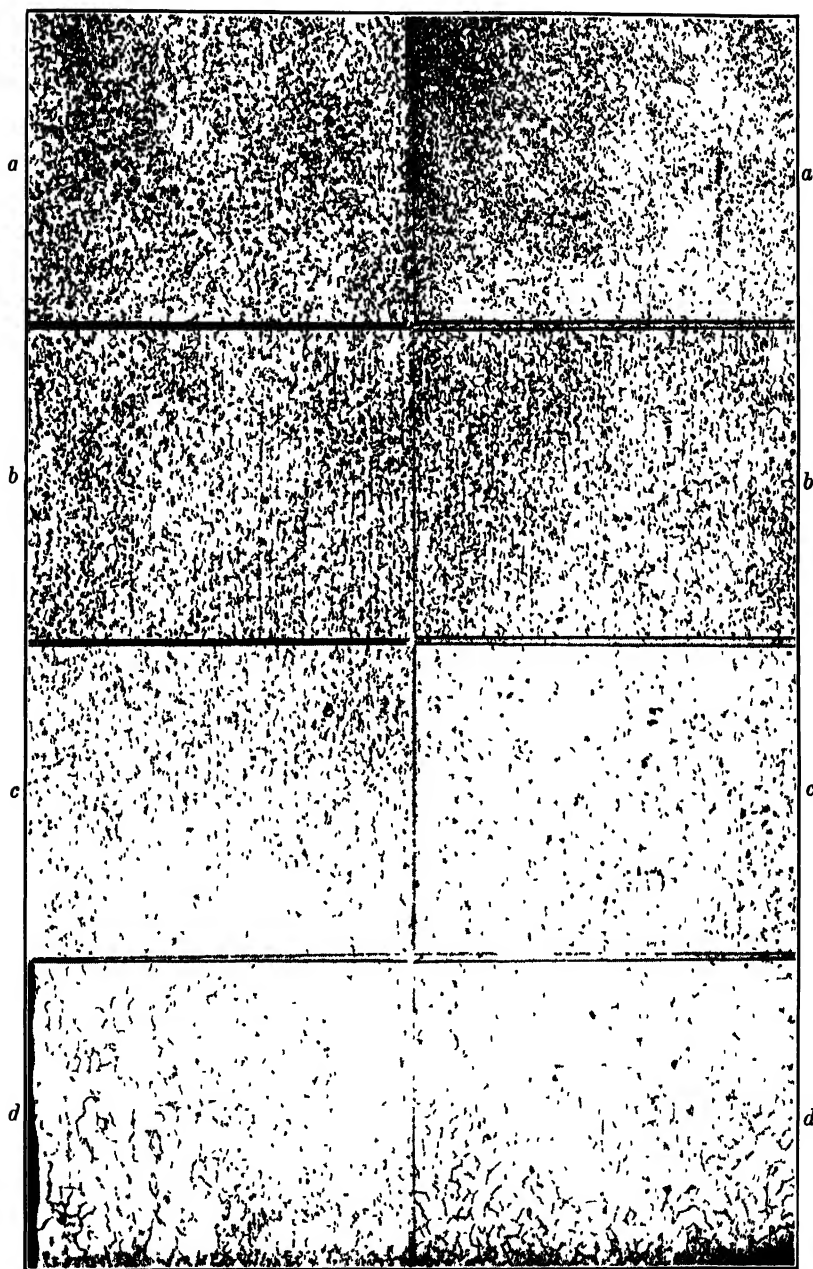


FIG. 9.—AS RECEIVED AND NORMALIZED STRUCTURES OF THE STEELS TESTED IN 0.062-IN GAGE. $\times 100$.

a. Cu-Ni-P steel.
b. Cu-Ni-P-Cr steel.

c. Cu-Ni-Cr steel.
d. Cu-bearing steel.

free bend and then bending flat. The impact tests were made by machining a specimen similar in size to the standard Charpy bar but of the thickness of the sheet and machining the standard Charpy keyhole notch. The values reported are those obtained, multiplied by the ratio of the thickness of the standard Charpy bar to the thickness of the sheet.



FIG. 9.—(CONTINUED.)
e. Plain carbon steel.

There appeared to be no “buckling” of even the thin 0.062-in. gage sheet under the blow of the hammer.

The sheets should be compared in the normalized condition to eliminate variations due to finishing temperature in rolling and to differences in heat-treatment. The tensile properties of the selected composition A are good (Table 10).

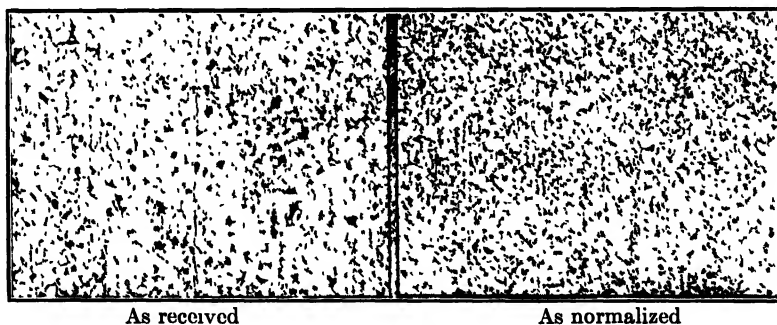


FIG. 10.—AS RECEIVED AND NORMALIZED STRUCTURE OF 0.125-IN. GAGE SHEET OF SELECTED COMPOSITION A, CU-NI-P STEEL. $\times 100$.

In all the 0.062-in. gage sheets as hot-rolled the elastic ratios were considerably higher than after normalizing, although the bend properties were better after normalizing. This indicates that a high elastic ratio obtained by “cold-working” in rolling is of no benefit with respect to bend properties. A normalizing treatment which lowered the elastic

ratio by removing working strains improved the bend properties, despite the fall in elastic ratio. In the 0.250-in. gage sheets of selected composition A, the hot-rolled sheet had a lower elastic ratio than the normalized sheet. This was no doubt because the higher finishing temperature in rolling gave a coarser grain in the relatively heavier sheet. After normalizing, the grain was finer (Fig. 11), and a better elastic ratio and better bend and impact properties were obtained.

The impact properties of all the steels were good (Table 10), even when tested at temperatures as low as -40°C. , the energy absorbed

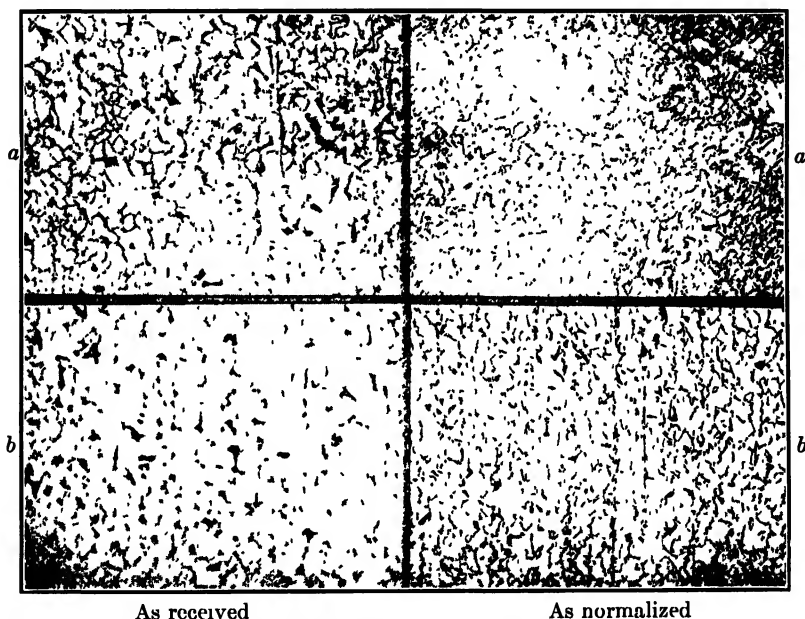


FIG. 11.—AS RECEIVED AND NORMALIZED STRUCTURES OF THE STEELS TESTED IN THE 0.250-IN. GAGE. $\times 100$.
 a. Cu-Ni-P steel.
 b. Cu-Ni-P-Cr steel

being amply high to insure a ductile type of fracture; silky or otherwise ductile fractures were, in fact, obtained.

Variation with Gage.—The variation in tensile properties and hardness with gage is an important consideration with the low-alloy steels. As indicated in Table 11, selected composition A showed very little variation in tensile properties with gage.

Effect of Time and Temperature of Normalizing.—Normalizing has the twofold effect of removing hot-rolling strains and refining the grain size. To remove hot-rolling strains and form an equiaxed grain, it is better to use a higher normalizing temperature and to heat for a longer time. On the other hand, this may cause grain coarsening and a lowering of the yield strength and elastic ratio (Table 12 and Fig. 12). The yield

strengths and elastic ratios decreased with increasing normalizing temperature and time at temperature because of the increase in grain size.

Effect of Aging.—The selected copper-nickel-phosphorus steel can obviously be strengthened by an aging treatment of air-cooling followed by reheating to about 1000° F., as in all copper steels with over 0.5 per cent copper. However, where the steel is to be welded or hot-formed the strengthening effect of aging would be lost. Moreover, as Lorig²⁶ indicates, the corrosion resistance of copper steels may be lowered by an aging treatment. On the other hand, for some uses the benefit of age-hardening could be utilized. From the standpoint of commercial heat-treatment it is, therefore, worth knowing how sensitive the reheating treatment is

TABLE 11.—*Variation in Tensile Properties and Hardness with Gage of Sheet of the Selected Composition*
NORMALIZED CONDITION

Designation	Type Composition	Gage, In.	Yield Strength, Lb per Sq In	Tensile Strength, Lb per Sq In.	Elastic Ratio	Elongation, Per Cent in 8 In	Rockwell B Hardness
A	Selected composition Cu-Ni-P.	0 062	61,500	75,000	0 82	22	84
		0 125	62,500	74,500	0 84	25	82
		0 250	60,250	72,000	0 83	25	83

TABLE 12.—*Effect of Normalizing Time and Temperature*
SELECTED STEEL A —COPPER-NICKEL-PHOSPHORUS. 0.125-IN. GAGE SHEET

Condition	Yield Strength, Lb per Sq In	Tensile Strength, Lb per Sq In	Elastic Ratio	Elongation, Per Cent in 2 In.	Reduction of Area, Per Cent
As rolled	69,000	78,000	88 5	29 5	55 0
Normalized 1650° F., 5 min . .	65,000	78,500	83 0	33 0	66 0
Normalized 1650° F., 10 min . .	61,500	75,500	81 5	32 0	65 0
Normalized 1650° F., 30 min .	57,000	74,000	77 0	32 0	60 0
Normalized 1800° F., 3 min ..	62,500	75,000	83 5	32 0	59 0
Normalized 1800° F., 5 min	59,000	73,500	80 0	31 5	60 0
Normalized 1800° F., 10 min . . .	58,500	74,000	79 0	32 0	57 0

to time of heating and how much loss of ductility there is after the maximum age-hardening.

Accordingly, aging tests were made of $\frac{3}{4}$ by 1-in. bar stock and 0.125-in. gage sheet of the selected composition A. The results are shown in Figs. 13 and 14 respectively.

Normalizing at 1650° F. followed by reheating at 1000° F. caused a material rise in the yield strength of the $\frac{3}{4}$ by 1-in. bar over the normal-

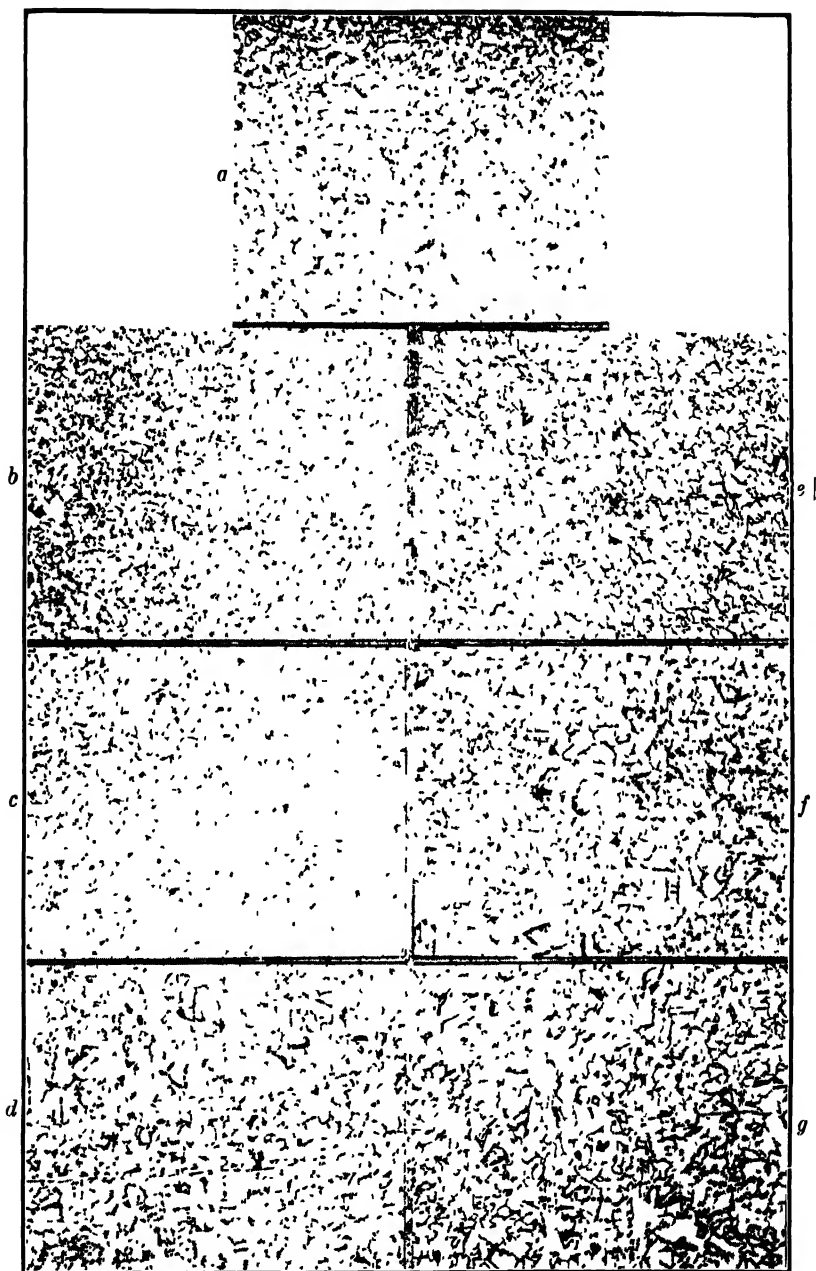


FIG. 12.—EFFECT OF TEMPERATURE AND TIME OF NORMALIZING SELECTED COMPOSITION A. 0.125-IN. GAGE SHEET.

a. As received.

b, c, d. Normalized at 1650° F. 5, 10, 30 minutes, respectively.

e, f, g. Normalized at 1800° F. 3, 5, 10 minutes, respectively.

ized condition (Fig. 13); the maximum rise of about 15,000 lb. per sq. in. was after about 6 hr. heating; this fell to about 10,000 lb. per sq. in. after about 12 hr.; longer heating up to 24 hr. caused only a slight further fall. Evidently after about 12 hr. heating the aging treatment is not

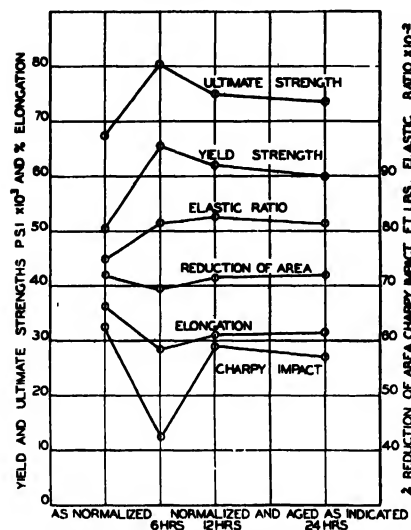


FIG 13.—TENSILE AND IMPACT PROPERTIES ON AGING $\frac{3}{4}$ BY 1-INCH BAR STOCK OF SELECTED COMPOSITION A

Normalized at 1600° F. and reheated at 1000° F. for the time intervals indicated

in yield strength of about 18,000 lb. per sq. in. after 2 hr. heating. After 12 hr. heating this had decreased to about 13,000 lb. per sq. in., after which there was a further gradual decrease with time of heating. The repeated bend values were not materially lowered at the stage of maximum age-hardening, and after 12 hr. aging were about as high and even somewhat higher than in the normalized condition. The rise in the elastic ratio upon aging was appreciable.

TABLE 13.—Charpy Impact Values of $\frac{3}{4}$ by 1-in. Bar of Selected Composition A

Condition	Testing Temperature, Deg C			
	23	0	-25	-40
	Impact Resistance, Ft-lb			
As rolled....	46 8	39 7	39 2	34 6

Impact Tests at Lowered Temperature.—There was virtually no fall in the impact resistance of the sheet specimens of the selected composition

A (up to 0.250 in. thick) with lowered temperature down to -40°C . (Table 10). In the $\frac{3}{4}$ by 1-in. thick material in the as-rolled condition,

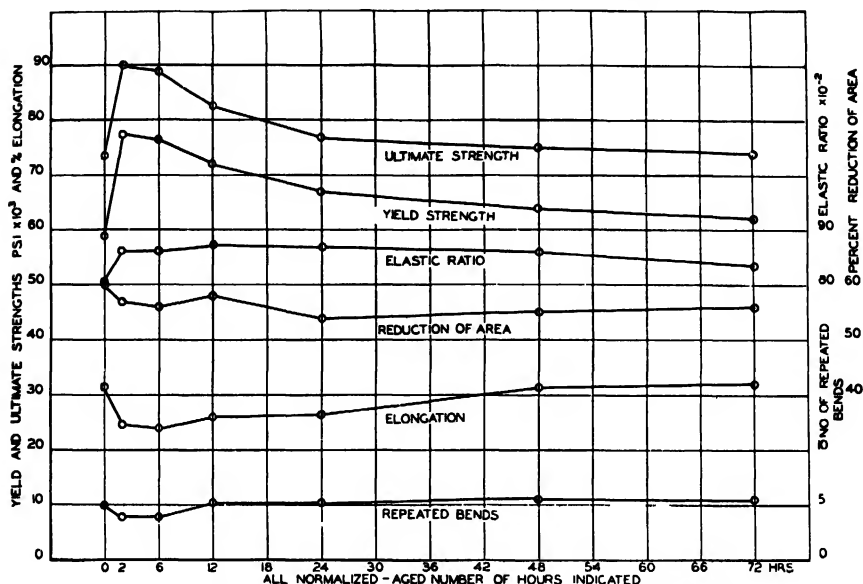


FIG. 14.—TENSILE AND BEND PROPERTIES OF 0.125-IN. GAGE SHEET OF SELECTED COMPOSITION A

Normalized at 1800°F . and reheated to 1000°F . for stated time intervals.

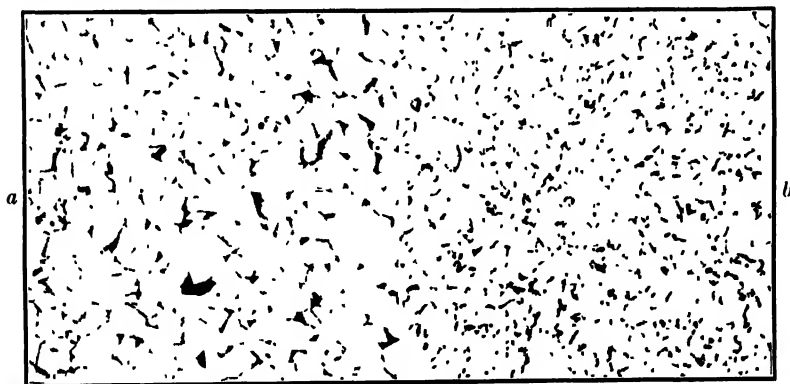


FIG. 15.—STRUCTURE OF $\frac{3}{4}$ BY 1-IN. BAR OF SELECTED COMPOSITION A. $\times 100$

a. As rolled.
b. Normalized.

however, there was a slight fall (Table 13) at -40°C . (though this was not appreciable).

Fatigue Properties.—The endurance limit of the $\frac{3}{4}$ by 1-in. bar stock as-rolled of selected composition A was determined, using an R. R. Moore rotating-beam fatigue-testing machine. The endurance limit was found to be 49,000 lb. per sq. in. (Fig. 16). The tensile strength was 67,750 lb.

per sq. in., giving an endurance ratio endurance limit/tensile strength of 0.72. This is unusually high, the usual value for steels being about 0.5. As has been stated, the yield strength of this $\frac{3}{4}$ by 1-in. bar stock (49,750 lb. per sq. in.) as rolled was not so high as that of the sheet of this same composition, apparently because of a high finishing temperature.

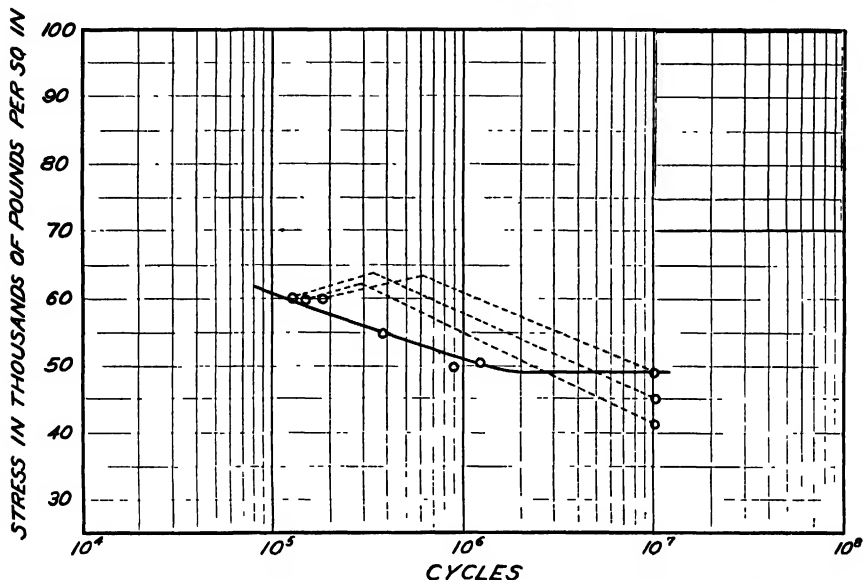


FIG. 16.—FATIGUE-TEST RESULTS OF $\frac{3}{4}$ BY 1-IN. BAR STOCK OF SELECTED COMPOSITION A IN THE AS-ROLLED CONDITION.
O, straight run.
O---O, stress raised after 10,000,000 cycles.

Welding Tests.—The sheets of the various steels were welded* by means of electric-arc and oxyacetylene welding and tensile, bend and impact tests of the welded joint were made. For the electric-arc welds $\frac{5}{32}$ -in. coated electrodes were used; the compositions of the rod and coating are as follows: welding rod, 0.17 per cent C, 0.46 Mn, 0.012 Si, 0.007 P, 0.029 S; coating on welding rod, 23.23 per cent SiO_2 , 0.51 Fe_2O_3 , 0.34 Al_2O_3 , 17.28 TiO_2 , 0.15 CaO , 5.65 MgO , 8.10 Fe-Mn , 4.60 Fe-Mo , balance organic binder.

Since the rods themselves are of plain carbon steel, evidently the molybdenum content of the coating is depended on for the attainment of high strength in the welded joint, and a pickup of as much as 0.40 per cent molybdenum by the fused-in metal may occur. The welding was done at about 30 volts and 120 amperes. For the gas welding, strips of the base material were used as welding rods. The welds were tested with the beads left on and with the beads ground off.

* Through the courtesy of the Columbus Bolt Works Co the welding was done by Mr. Frank Kidwell, the company's chief welder.

Tests with Beads Left On.—The results for the specimens with the beads left on are given in Tables 14 and 15. Full-sized tensile specimens of 8-in. gage length were cut from the welded sheet, the welded joint being

TABLE 14.—*Results of Mechanical Tests of Welded Joints of Commercial Low-alloy Steel Sheet. Arc Welds*
WELD BEADS LEFT ON

Material	Gage, In	Yield Strength, Lb. per Sq. In	Tensile Strength, Lb. per Sq. In	Elastic Ratio	Elongation, Per Cent in 8 In	Red of Area, Per Cent	Location of Fracture	Longitudinal Bend Tests	
								Degrees of Bend	Flat
A	0.062	70,000	78,000	0.90	10		In weld	180	OK
	0.062	68,500	79,500	0.86	18		Out of weld	180	Slight crack
B	0.062	60,000	80,000	0.75	10		In weld	180	Slight crack
	0.062	58,000	81,500	0.71	19		Out of weld	180	Slight crack
C	0.062	61,000	74,000	0.82	20		Out of weld	180	Slight crack
	0.062	61,000	74,000	0.82	22		Out of weld	180	OK
D	0.062	41,000	48,500	0.84	11		In weld	180	OK
	0.062	40,000	51,000	0.78	20		Out of weld	180	OK
E	0.062	44,000	53,000	0.83	17		Out of weld	180	OK
	0.062	40,000	51,000	0.78	19		Out of weld	180	OK
A	0.125	66,500	77,000	0.86	20	66	Out of weld	180	OK
	0.125	67,000	77,500	0.86	20	65	Out of weld	180	Weld cracked at junction
B	0.125	68,500	79,000	0.87	21	67	Out of weld	180	OK
	0.125	66,500	79,000	0.84	20	65	Out of weld	180	OK

in the center of the specimen, and tested in tension. Specimens of the same size were bent along the weld. As the specimens could not be made to bend in the weld itself because of the stiffer sections, the bending occurred directly adjacent to the weld. The specimens were first bent to 180° where possible and then flattened completely.

The electric-arc welds gave somewhat poorer results in the 0.062-in. gage sheet than in the heavier sheet (Table 14). Undoubtedly this was because the welder had difficulty in welding this thin sheet by the arc method using the rather thick $\frac{5}{32}$ -in. electrode, which was the only size of electrode available. These tests indicated that the selected composition is readily weldable by the arc method, forming sound, clean welds.

Of the gas welds, better welds were obtained on the thinner sheets by means of gas welding than by arc welding (Table 15).

Tests with Beads Ground Off.—The same type of tensile tests were made with the beads ground off as with the beads left on, and in addition impact tests of the sheet (as previously described) were made with the notches in the weld and directly adjacent to the weld. Rockwell hardness tests

TABLE 15.—*Results of Mechanical Tests of Welded Joints of Commercial Low-alloy Steel Sheet. Gas Welds*

Material	Gage, In	Yield Strength, Lb. per Sq In	Tensile Strength, Lb. per Sq In.	Elastic Ratio	Elongation, Per Cent in 8 In	Red of Area, Per Cent	Location of Fracture	Longitudinal Bend Tests	
								Degrees of Bend	Flat
A	0 062	68,000	79,000	0 86	15		Out of weld	180	OK
	0 062	68,500	80,000	0 86	16		Out of weld	180	OK
B	0 062	69,000	81,500	0 85	21		Out of weld	180	OK
	0 062	68,000	81,000	0 84	21		Out of weld	180	OK
C	0 062	61,500	74,500	0 83	17		Out of weld	180	Slight crack
	0 062	59,500	74,000	0 80	17		Out of weld	180	Slight crack
D	0 062	32,000	51,000	0 76	29		Out of weld	180	OK
	0 062	40,500	52,000	0 78	29		Out of weld	180	OK
E	0 062	42,000	50,000	0 84	9		Out of weld	180	OK
	0 062	41,500	50,000	0 83	12		Out of weld	180	OK
A	0 125	64,500	78,000	0 83	21	63	Out of weld	180	OK
	0 125	64,500	77,500	0 83	21	62	Out of weld	180	Cracked
B	0 125	65,500	80,000	0 82	19	66	Out of weld	180	Cracked
	0 125	64,500	78,500	0 82	20	62	Out of weld	180	Broke

of the ground-off specimens in the weld and directly adjacent to the weld were also made.



FIG. 17.—STRUCTURE OF METAL IN WELD OF GAS-WELDED 0.125-IN. GAGE SHEET OF SELECTED COMPOSITION A. $\times 100$.

Poor welds were obtained by arc-welding the 0.062-in. gage sheet, as was indicated by the tests with the beads left on (Table 16). In the 0.125-in. gage sheets, however, excellent welds were obtained by arc welding, as is indicated by the high impact properties in and adjacent to the weld down to testing temperatures of -25°C . It is of interest to point out that even in arc welding, where the same type of electrode was used on all the welds, the selected composition A showed somewhat less hardening in the welds (see Rockwell hardness data) than the other low-alloy steels tested. The lower hardenability of the selected composition A was quite apparent on gas welding.

Considerably better gas welds were obtained in the 0.062-in. gage sheets

TABLE 16.—Results of Mechanical Tests of Welded Joints of Commercial Low-alloy Steel Sheet. Arc Welds
WELD BEADS GROUND OFF

Ma- terial	Gage, In	Yield Strength, Lb per Sq In	Tensile Strength, Lb per Sq In	Elastic Ratio	Elonga- tion, Per Cent in 8 In	Red of Area, Per Cent	Location of Fracture	Impact Tests, Ft-lb						Rockwell B Hardness	
								Notch in Weld			Notch Next to Weld			In Weld	Next to Weld
								23° C	0° C	-25° C	23° C	0° C	-25° C		
A	0 062 0 062		59,000 73,500		0 1		In weld In weld	13 7 26 9	26 9	11 9	30 4	26 9	28 7	94	89
B	0 062 0 062		64,500 61,500		1 1		In weld In weld	15 2 24 2	24 2	6 1	29 3	28 7	26 9	95	86
C	0 062 0 062		45,500 45,500		0 0		In weld In weld	23 2 16 2	16 2	5 8	33 0		37 1	95	86
D	0 062 0 062	40,500 41,000	51,000 51,500	0 79 0 80	26 25		Out of weld Out of weld	32 0 28 3	30 0 24 0	21 3 12 9	31 3 29 0	31 9 29 0	29 4 29 0	87	61
E	0 062 0 062	39,500	42,000 35,000		3 0		In weld In weld	28 3	24 0	12 9	29 0	29 0	29 0	87	64
A	0 125 0 125	66,000 65,000	75,500 78,000	0 87 0 83	12 2	41 27	Out of weld In weld	26 2	22 7	Defect in weld 6 1	26 8	24 8	21 2	91	86
B	0 125 0 125	68,000 65,000	79,500 65,000	0 86	19 13	61 21	Out of weld In weld	17 4	27 5	13 0	36 5	28 8	23 9	93	87

TABLE 17.—Results of Mechanical Tests of Welded Joints of Commercial Low-alloy Steel Sheet. Gas Welds
WELD BEADS GROUND OFF

Ma- terial	Gage, In	Yield Strength, Lb per Sq In	Tensile Strength, Lb per Sq In	Elastic Ratio	Elonga- tion, Per Cent in 8 In	Red of Area, Per Cent	Location of Fracture	Impact Tests, Ft-lb						Rockwell B Hardness	
								Notch in Weld			Notch next to Weld			In Weld	Next to Weld
								—25° C			0° C				
								23° C	0° C	—25° C	23° C	0° C	—25° C		
A	0 062 0 062	66,500 66,500	75,000 66,500	0 89 0 89	7 3		In weld In weld	26 3 25 5	28 0 24 2	22 1 22 4	25 4 33 0	31 0 33 9	22 1 30 9	95 93	85 85
B	0 062 0 062	69,000 65,000	76,000 47,500	0 91 0 89	8 0		In weld Out of weld	25 5 33 0	24 2 31 3	22 4 25 5	33 0 35 3	33 9 37 1	30 9 35 9	93 94	85 86
C	0 062 0 062	65,000 65,000	73,000 73,000	0 89 0 89	19 20		Out of weld In weld	28 0 33 6	28 9 36 4	36 9 30 3	34 5 32 7	30 2 35 8	28 9 32 7	89 66	58 53
D	0 062 0 062	38,500 39,000	45,500 50,500	0 85 0 77	8 19		In weld In weld	30 0 17 3	12 7 10 8	12 7 12 4	25 4 43 0	32 4 36 4	24 2 23 0	90 96	83 86
E	0 062 0 062	39,000 39,000	45,500 43,500	0 86 0 90	6 2		In weld In weld	30 0 17 3	12 7 10 8	12 7 12 4	25 4 43 0	32 4 36 4	24 2 23 0	90 96	83 86
A	0 125 0 125	65,000 66,000	73,000 73,500	0 89 0 90	17 9	48 20	Out of weld In weld	30 0 17 3	12 7 10 8	12 7 12 4	25 4 43 0	32 4 36 4	24 2 23 0	90 96	83 86
B	0 125 0 125	66,000 64,000	66,000 78,000	0 82 0 82	1 8	7 11	In weld In weld	17 3 17 3	10 8 10 8	12 4 12 4	43 0 43 0	36 4 36 4	23 0 23 0	96 96	86 86

than in the arc-welded sheets of this gage (Table 17). In the 0.125-in. gage sheets good welds were obtained on all of the steels. The selected composition A, showed good impact resistance in and outside of the welds down to a testing temperature of -25°C .

The low hardenability in welding of the selected composition A is well illustrated in Fig. 17, showing the microstructure in the weld of a gas-welded 0.125-in. gage sheet.

SUMMARY

1. The properties desired in low-alloy high-strength steels are a yield strength of about 60,000 lb. per sq. in., formability closely approaching that of plain carbon structural steel, good weldability and considerably greater atmospheric corrosion resistance than plain carbon steel.

2. To get the full benefit of the low-alloy high-strength steels, the yield strength and not the tensile strength should be used as a basis of design. For a certain increase in yield strength of low-carbon steel by means of an alloying addition, better bend test values—that is, formability—are obtained the smaller the accompanying increase in tensile strength. Thus, air-cooled low-alloy steels with a higher elastic ratio will have better bend properties for a given yield strength, say 60,000 lb. per sq. in., than steels with a lower elastic ratio.

3. The ordinary alloying elements with iron are grouped according to their effect on the elastic ratio. Carbon, manganese, chromium, silicon and molybdenum tend to raise the tensile strength at a considerably faster rate than the yield strength and thus to give lower elastic ratios. Copper, phosphorus and nickel raise the tensile strength at a slower (or equal) rate than they do the yield strength and thus give higher elastic ratios.

4. Data are given indicating that the use of the elements copper, phosphorus, nickel in the low-alloy high-strength steels gives more desirable mechanical properties than the use of the elements carbon, manganese, chromium, silicon and molybdenum.

5. Since (1) copper, phosphorus and nickel also raise the corrosion resistance (nickel being used to overcome the occurrence of checking during rolling of copper steels), and (2) when they are used in the proper proportion they give good weldability without causing detrimental air-hardening from the welding heat, it appears logical to use them as the basis for a low-alloy high-strength steel composition.

6. Mainly on the above premises, the following low-alloy high-strength composition was chosen: C, 0.10 per cent max.; Mn, 0.50; Si, 0.15; Cu, 1.00; Ni, 0.5; P, 0.12.

7. Results of mechanical tests of commercial sheet made of the selected composition are given, indicating that the mechanical properties of this

low-alloy steel are satisfactory. The selected composition showed high impact resistance at atmospheric temperatures and down to -40°C. , both in sheet and in $\frac{3}{4}$ by 1-in. bar stock. After age-hardening the impact resistance remained high—over 40 Charpy. Fatigue tests of the selected composition showed it to have the unusually high endurance ratio $\left(\frac{\text{endurance limit}}{\text{tensile strength}}\right)$ of 0.72.

8. Results of tests of arc and gas welds of commercial sheet of the selected composition are given. The selected composition showed good weldability and only slight hardening on air-cooling from the welding heat. Tests in the weld and directly adjacent to the weld in both arc and gas welds showed high impact resistance down to -25°C.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to the Inland Steel Co., which sponsored this work, for permission to publish the results. Acknowledgment is also made to Messrs. T. S. Washburn and J. F. Woschitz of the Inland Steel Co., and to Mr. C. E. Williams, Dr. H. W. Gillett, Dr. O. E. Harder, and Messrs. H. E. Johnson, A. L. Sanford, C. T. Greenidge, H. B. Kinnear, W. A. Welker, Jr., of Battelle Memorial Institute, for advice and aid in the study.

Much of the fundamental information on the effects of copper in steel was obtained in work at Battelle Memorial Institute for the Copper and Brass Research Association, and that on the effects of phosphorus in work sponsored by the Swann Research Corporation.

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DISCUSSION

(Erle G. Hill presiding)

E. E. THUM,* Cleveland, Ohio.—The remarks I am going to make are not in any sense derogatory to the excellent work the authors have done, or of the quality of the steels they have developed, but I do question one or two things that have been stated more or less dogmatically. Dr. Epstein said, perhaps off the record, that quenched and tempered steel is the best condition a steel can be in. I think we ought not to let that go by without challenging, because we can think of cold-drawn wire, for instance, as being much better for many purposes in the cold-drawn condition than in the quenched and tempered condition. Even some alloy steels may have optimum fabrication and service properties when annealed—5 per cent chromium tubing, for instance.

Also, I should like to question the somewhat broad statement that yield point is the figure in which designers are most interested. Maybe the statement was not made in exactly those words, but that was the inference. I doubt whether designers generally are interested in the yield point as widely as one might infer from that statement. Most of them are still relying to a great extent upon the ultimate strength and I think will continue to do so for a long time, or at least until the matter of yield point is better standardized by our friends, the testing engineers. There is too much of a personal element, I believe, in the determination of yield point or yield strength or elastic limit or Johnson limit. Under those circumstances, a careful designing engineer cannot be blamed for questioning values of "yield point" as ordinarily published. Our English brothers are getting around the problem gradually by specifying proof strength—that is, tensile stress required for a specified small amount of elongation. One wonders just how this enters the calculations in formulas based on elastic action, but the plan has at least the advantage of specifying exactly what is meant, which is more than we know usually when we say "yield strength." Some of the very best and toughest materials have no yield point at all, and possibly no true proportional limit. They may even act plastically almost from the very beginning of stress.

I am also interested to note that phosphorus, as well as copper, is no longer regarded by some as the big bad wolf it used to be a few years back. I can recall a very extensive and expensive investigation that came up during the war on permissible phosphorus and sulfur in various carbon steels. At that time phosphorus was thought to be an unmitigated nuisance; in years preceding that the exhaustion of low-phosphorus and sulfur ores caused an entire revision in the manufacturing operations of the whole American steel industry from the Bessemer to the open-hearth process. Perhaps after we learn enough about it, we will come to the conclusion that sulfur has its uses as well as phosphorus.

H. L. MILLER,† Massillon, Ohio (written discussion).—This paper builds up a strong case for the addition of copper and nickel, with copper the predominating element. However, the reasons advanced for the addition of phosphorus, instead of molybdenum as a third element, are not as convincing to the writer.

In Table 7, steel No. 1 and steel No. 3 compare as shown on 0.125-in. gage normalized sheets. This shows a jump of only 2000 lb. in yield point with an increase of 6500 lb. in tensile due to increased phosphorus, with a drop of four points in elastic ratio. On the face of these values it is rather confusing to say that the effect of phosphorus is to increase yield point and elastic ratio as shown in Table 8, which shows a

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jump of 9000 lb. in yield and tensile due to phosphorus in the selected analysis. The results shown in Table 8 seem to be somewhat in conflict with those in Table 7.

In 1925, F. F. McIntosh⁴³ advanced rather wide claims for phosphorus as a "reformed crook" one might say in regard to its presence in steel. This argument was rather neatly answered by R. T. Rolfe⁴⁴, of Bedford, England, member of the Steel Research Committee of the I.A.E. and S.M.M.T. We believe that in regard to plain carbon steels phosphorus must be regarded with considerable conservatism. The effect of additions of nickel and copper plus deoxidation of the steel may counteract the effect of the phosphorus on shock resistance to some extent in freshly rolled and normalized steel. In regard to the subject of aging at room temperatures, many authorities claim a relationship between phosphorus and nitrogen content in the process of aging or embrittlement.

In a previous paper by Dr. Epstein⁴⁵, we find this statement: "It may be assumed perhaps since the amount of phosphorus present is considerably below its accepted solubility limit, that this element does not itself precipitate, but causes nitrogen (or rather a compound of nitrogen and iron), for example, to precipitate along certain preferred planes in the crystal, causing more ready cleavage and consequent brittleness."

With this statement in mind, and remembering that many processes involved in fabrication of tanks, railroad cars, etc., are comparable to the short time reheating in galvanizing cold-punched sections, we should like to ask Dr. Epstein what would be the effect of still further increasing phosphorus to a point nearer its solubility limits and a more emphasized reaction with nitrogen compounds necessarily present in his selected analysis? We would also refer to an article by F. Rogers⁴⁶. F. H. Andrews, in a discussion of that article (p. 621) stated that in a series of six steels with varying phosphorus from 0.018 to 0.152 with carbon 0.35, Mn 0.45, Ni 3.50, treated by oil quench and tempered at 650° C, cooled slowly, the low-phosphorus steel gave an impact of 90 ft-lb and the 0.152-phosphorus steel a value of only 1 ft-lb. This seems to indicate that even 3.5 per cent nickel was not sufficient to overcome the embrittling effect of the phosphorus.

With regard to the high phosphorus content of wrought-iron bars, we should like to raise the question as to what percentage of the total phosphorus is found in the slag as compared with the amount in the ferrite. It is commonly accepted that the ferrite in wrought iron is the purest commercial grade of ferrite, and if the phosphorus content is mainly in the slag, wrought iron could not be cited as an example of a high-phosphorus material.

The producer of high tensile steels must bear in mind that the only important field of application, large enough to absorb sufficient tonnage to warrant the expense of development of high tensile sheet, is in the railroad car construction and repairs.

The light-weight passenger equipment is gravitating toward welded construction, and ductility and shock resistance in the as-welded condition are of primary importance in this field. Corrosion resistance is not so important, as the cars are always painted outside. Tonnage on this particular field is, for some time to come, a spasmodic demand. Box cars spend too much time on foreign lines to warrant the payment, by most railroads, of the higher cost for light-weight construction. The field in this particular case is very limited. Open-top cars, such as mill-type gondolas

⁴³ Carnegie Inst. of Tech. *Bull.* 25.

⁴⁴ *Min. & Met.* (Dec., 1926) 578.

⁴⁵ S. Epstein: Embrittlement of Hot Galvanized Structural Steel. *Proc. Amer. Soc. Test. Mat.* (1932) 32, pt. II, 293.

⁴⁶ F. Rogers: Phosphorus in Nickel, Chrome and Other Steels. *Jnl. Iron and Steel Inst.* (1920) 101, 613-625.

without bottom doors, are exposed to the elements at all times and often to corrosive ladings. Tight-bottom cars also have water standing on the bottom plates and rust out rather rapidly. Time may show that a steel with atmospheric corrosion about three times that of copper-bearing steel and applicable in plates $\frac{3}{16}$ in. thick instead of $\frac{5}{16}$ -in. common steel will be economically feasible, but to floor a 40-ft. gondola in $\frac{5}{16}$ -in. alloy steel at standard prices for these steels would cost the railroad company about \$135 more per car. The average life of this type of car bottom in copper-bearing steel is 15 years, and to carry the additional \$135 for 15 years before the alloy steel would begin to earn its place is asking too much of almost any engineer, especially as the life of these steels over a long span is still more or less a matter of conjecture. Rates of rusting on railroad cars are often inexplicable. During the depression, cars in storage have rusted out in three years and have had to be scrapped, while other cars of the same series kept in regular service are still in good condition. The gondola car is seldom loaded to capacity and the weight saving of 8000 lb., which is possible in steel of 70,000 yield point, is seldom reflected in increased pay load and generally shows only the lighter drag on the engine in its favor.

But the steel coal-hopper car is a piece of equipment that offers the greatest field for alloy steel sheets and plates. To successfully withstand the service conditions to be met in hauling and often storing high-sulfur coals in steel cars, the steel, if used in lighter sections, must have greatly superior resistance to the dripping of a 1 to 5 per cent sulfuric acid solution.

Laboratory tests are often confusing, especially in attempting to correlate them to service results, but the copper-nickel-molybdenum steels submerged in either 4 or 20 per cent sulfuric acids show much higher resistance to solution than the steels containing high phosphorus. A large coal-truck body in service in Chicago hauling coal in regular service for two years shows no sign of corrosion or pitting, and the steel contains 1.50 per cent copper and 0.18 molybdenum. Common steel bodies operated by this company require repairs at about two years in service.

A steel to resist successfully the coal-car conditions must have both atmospheric-rust resistance and as much acid resistance as is commercially feasible. Tests of coal cars in operation, or soon to be placed in operation, should tell us within the next two or three years which analyses will be commercially applicable.

This discussion, while departing somewhat from the strictly technical side, is presented with the hope that it may somewhat clarify our real objectives in making and selling high-strength steels and to show the relations between our objectives and the metallurgical methods of gaining them.

F. M. WALTERS, JR., * Youngstown, Ohio —The authors of this paper are to be congratulated on the extensive survey of the various properties of the steel of selected composition. When a new steel is put on the market, the variety of information demanded by the customer is astonishing. Data are requested on such unusual properties as electrical resistance and thermal conductivity. The authors have given a very interesting picture of the line of reasoning that led them to the selection of a particular composition for a high-strength steel. Some applications require high yield strength combined with good welding characteristics, other applications require good formability. Both the elastic ratio and the repeated bend test may be questioned as universal and conclusive methods for evaluating the workability of a particular composition of steel. Experience with deep drawing indicates the desirability of a low elastic ratio. I am sure that the authors do not wish to carry the principle of high elastic ratio to its logical conclusion and an elastic ratio of one, with the yield strength equal to the ultimate strength. In general, workability depends upon ductility, but

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the criterion of ductility depends upon the particular cold-forming operation under consideration. Table 10 reveals that for the steels studied the steels with the lower elastic ratios show the better repeated bend tests. This contradiction may lie in the determination of the yield strength of the thinner material, since in 16 and lighter gage material, the accurate determination of the yield point is extremely difficult.

J. STRAUSS,* Bridgeville, Pa.—High endurance ratio, after all, is a rather frequently encountered property in the low-carbon, low-alloy steels when they are well made. I wonder whether the value is real or fictitious. In other words, would we not obtain more information upon what this value actually means if we were to measure the properties of the steel after the endurance test has been made, and particularly the properties (including hardness) at the point of rupture? I think it would be very enlightening.

Dr. Epstein made a selection of a final composition based upon a preliminary examination of the influence of individual alloy metals and an admittedly arbitrary combination of the information thus obtained. I have been studying steels of this particular composition type for about four years, and I submit that there are good combinations of the copper, nickel and phosphorus in steels both with low silicon and with relatively high silicon in which the copper-nickel ratio differs materially from that which Dr. Epstein has selected. This comment is not to be interpreted as derogatory but merely as indicating that other ratios are highly useful in obtaining the properties that he originally set out to obtain in his investigation.

B. D. SAKLATWALLA,† Pittsburgh, Pa.—This paper may possibly create an impression that might become very misleading to those who have not actually dabbled in the field of low alloys. I am stating this from experience I have gathered in my work in this field since approximately 1920. It would be dangerous to evaluate the effect of a combination of elements from the effect of the individual elements. We have known for a long time the effect of the single elements; for instance, the effect of copper on the yield point has been well known. There might be a danger in concluding that if a higher yield point is desired in a steel with a number of elements an increased copper content will produce it, because that is not necessarily so.

The effect of the addition of chromium to the particular composition discussed by the authors—namely, that the elastic ratio is pulled down—brings out very clearly the fact that elements in combinations do not behave in the same way as when used singly in conjunction with carbon. We all know that such would not be the case with chromium when used in carbon steels and therefore what chromium or any other element will do when in the presence of other alloying elements can only be determined in each particular case.

The same reasoning applies to phosphorus. The effect of phosphorus described by Mr. Miller may be applicable only to that particular type of steel, but when the phosphorus content is applied to another type of combination it gives an entirely different steel, so that it may be proper to state that these elements in combinations produce effects not only different in degree but in quality.

I would like to know from Dr. Epstein something about the origin of the steels tested by him; whether they were from laboratory heats or from large commercial heats. In these complex steels the effects of residual elements, like nitrogen, oxygen, and the like, might have a very important influence. The influence of such elements would be especially marked in the presence of phosphorus. All these factors would have to be considered in getting down to the fine points in drawing general conclusions

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as to the importance of merely raising the yield point by means of one or the other alloying element.

W. E. BUCK,* Granite, Ill.—Mr. Strauss brought out one point that has bothered me a great deal as to what the effect of the higher phosphorus will be after the steel has been in service for some time and subjected to reversal of stress near the yield point. Several years ago, our firm was badly hit by a lot of plain carbon steels of high phosphorus content, which failed after they were stamped. The stampings were 100-lb. white lead kegs; after several months in storage, the kegs began to split. They had been filled with white lead and it became an expensive proposition both for ourselves and for the lead company. Some of those kegs split in as many as 13 strips as straight as though they had been sheared. In some in which the higher phosphorus material was used, the defect appeared immediately, but some on the borderline were filled and sent out.

In the handling of these steels in car and tank construction, especially tank construction where there is "tick-tack" on the heads of the tanks and reversals of that sort, may there not develop a cold-hardening effect that will be very detrimental over a long period, although the data presented by Dr. Epstein and his coauthors do not indicate that that is true at all with these compositions.

S. L. HOYT,† Milwaukee, Wis.—We have been hearing a good deal about these low-alloy steels for several years, but the source of the information has been mainly through advertisements in trade journals plus contact with sales representatives. We can place much reliance in advertising that appears in the technical press, but at the same time the amount of information that can be given through media of that kind is necessarily limited. Battelle Memorial Institute and the Inland Steel Co. are to be congratulated for publishing their information so freely. To my knowledge, it is the only attempt to give a comprehensive review of these low-alloy steels. From the standpoint of the consumer, I feel that is an extremely important, even necessary, thing to do if these steels are to be put into service as rapidly as their peculiar merits and properties warrant.

During the discussion the question of using the yield strength instead of the tensile strength was brought up, to use as the basis for the factor of safety. Probably that should be discussed more than it has been. While it seems that the yield strength can be used, it is also true that engineers also base their design values on the tensile strength.

S. EPSTEIN, J. H. NEAD AND J. W. HALLEY (written discussion).—In regard to the point brought up by Mr. Thum and Dr. Hoyt, of using the yield strength as the basis of design, we believe that the argument for this as presented in the paper is sound. The difficulty of accurately determining the yield strength of various commercial steels or of the lack of a standard test method is a different problem (one for the testing engineers) which the authors are not attempting to solve. It is possible to determine the yield strength fairly accurately in the research laboratory, particularly where a definite drop in the beam is obtained, as occurred in these steels. On the basis of the argument presented in the paper, therefore, one can, from the research and development standpoint, choose certain compositions in preference to others because they tend to give a higher yield strength for the same tensile strength. This does not mean that in testing such steels commercially the engineer must necessarily determine the yield strength, although with these steels the yield strength is readily determined. He can still make any test he desires, but irrespective of the testing method the steel will have a high yield strength if the composition has been properly chosen.

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Mr. Thum has brought up the interesting question whether a quenched and tempered steel is the best kind of steel. Be that as it may, the point we wish to make is that a high elastic ratio in medium-strength structural steels is accompanied by higher reduction of area and higher impact resistance, these highly desirable properties being characteristic of quenched and tempered steels. By choosing the proper composition, it is possible to obtain characteristics after normalizing similar to those which are valued, no doubt rightfully, in the quenched and tempered steels.

Mr. Miller questions the advisability of using a high phosphorus content. We, of course, agree that in plain carbon steel and wrought iron, in heavy sections, phosphorus has been considered a dangerous element. At the same time, however, from a research standpoint, we should not let the experience of the past frighten us from using phosphorus, if metallurgists have learned how to avoid its harmful effects. If we have learned how to deoxidize steel so that higher phosphorus contents can be used with impunity, why should we allow the old experiences with phosphorus before this was known stop us from using it? The data in the paper indicate that the higher phosphorus steel sheets tested had good ductility and shock resistance, both before and after welding. This should also answer Mr. Buck's discussion. Thus a properly deoxidized steel will show little or no embrittlement on aging. Mr. Miller also brings up the effect of phosphorus on corrosion resistance, both atmospheric and against 1 to 5 per cent sulfuric acid solutions as encountered in coal cars. The subject of corrosion resistance is admittedly uncertain, no adequate data being available. All we can do now is to await the results of experience and corrosion tests. Against atmospheric corrosion, at least, phosphorus seems to be definitely beneficial.

Dr. Walters questions whether a high elastic ratio is a good merit index for steel. In the restricted sense used in the paper for formable medium-strength structural steels in the normalized condition it appears to be. As mentioned in the paper, a high elastic ratio, while probably desirable for good bend properties, is probably undesirable for good deep-drawing properties. Much more work is required before more definite statements can be made. It appears to be true, however, that for a certain yield strength, say 60,000 lb. per sq. in., better bend properties will be obtained with steels of lower tensile strength than with those of higher tensile strength.

Mr. Strauss and Dr. Saklatwalla have both emphasized that generalizations based on simple steels cannot always be translated to complex steels. Of course, this is true. We feel, however, that the selected composition is simple enough so that the generalization in regard to the high elastic ratio drawn from the binary alloys applies in the main to this steel. Whether equally favorable elastic ratios can be obtained with other elements or other combinations of elements remains to be determined. The carbon content and the manner of deoxidation, no doubt, also play an important part.

Mr. Strauss mentioned the high endurance ratio and suggested finding out whether these steels with a high endurance ratio also show a low susceptibility to notch effects and to overstresses. It would be of interest to determine the damage line of the steels of high elastic ratio.

J. STRAUSS.—I am not especially concerned with that, but rather with the hardness at the point of fracture. In other words, the tensile strength of sound, soft steels at the end of the endurance test may be materially different from what it was at the beginning of the test.

S. EPSTEIN.—Would it not be of interest if the steel has a high endurance ratio?

J. STRAUSS.—A high endurance *limit* is of course of great value *if it does not exceed the true elastic limit*. As to the damage line I am not in entire agreement with the work thus far done upon that subject.

The Metallurgy of "Pure" Iron Welds

By GILBERT E. DOAN,* MEMBER A.I.M.E., AND WILLIAM C. SCHULTE†

(New York Meeting, February, 1936)

AN extensive program of investigation is being carried out at Lehigh University in the study of arcs and arc welds of high-purity iron¹, sponsored by the Engineering Foundation. The part of that program reported in the present paper deals with welds made of high-purity iron in an argon atmosphere and for comparison with them welds made of the same iron in ordinary air. Welds of commercial steel also were made in argon and in air. The primary purpose of the study is to discover the basic physical constants of iron welds when not contaminated either by impurities in the iron or by the action of oxygen and nitrogen of the air during welding. Upon these constants can be founded such future studies as will determine what effects the various impurities and alloy elements present in steel have upon its welding characteristics, and what influence is exerted by the action of oxygen and nitrogen.

The welding of steel involves such a multitude of variables, both of composition and of procedure, that development in the fabrication of this most important metal has necessarily been slow, wasteful, and in many instances discouraging. In the present investigation, the simplest possible condition has been selected; namely, iron practically free from contamination and a nonparticipating atmosphere, the inert gas argon. This simplification reduces the number of variables to a point where more rigid control of the system is possible.

Although this study is significant for the contributions it makes to the science of steel fabrication, yet it is hoped that it will not be without value also in increasing knowledge of the nature and behavior of iron and steel in general. From the standpoint of open-hearth practice, and to some extent from the standpoint of electric-furnace practice also, the conditions of melting and casting iron in this investigation are extraordinary. The casting temperature is high, the mean temperature of the metal probably reaching 2000° C. (3600° F.)². The rate of chilling of

Manuscript received at the office of the Institute Nov. 29, 1935.

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this metal in the "mold"—that is, in the metal object being welded—is unusually rapid. The argon atmosphere, especially after the first few seconds of welding, is extremely pure. And the iron, both that of the electrode and of the plate, is of high purity. The "castings" produced under these new conditions may behave in ways that ultimately will enable us to understand more fully some of the many idiosyncrasies of iron and steel produced in present-day tonnage programs.

In passing it may be remarked that the arc itself is found to be quite a new phenomenon under these conditions of high purity. For example, it will not exist if the purity of the gas is carefully guarded, but rather goes out as soon as it is struck. The crater under the arc, the feature that is called "penetration" by the welder, simply does not exist under these conditions. Hence, welding is impossible. These aspects of the investigation have been described elsewhere; also the apparatus and the methods employed to obtain the welds¹. The present account deals with the metallurgical features of the metal before and after deposition by arc welding.

MATERIALS USED

The wires and plates used in this program were of carbonyl iron obtained from the I. G. Farbenindustrie, Ludwigshafen, in May, 1933. This material is formed when the gas iron carbonyl is heated, somewhat like the action of nickel carbonyl in the Mond process. The analysis given by the manufacturer is: sulfur, phosphorus, silicon, manganese, 0.000 per cent; carbon, 0.016 per cent. The oxygen content was understood to be below 0.01 per cent. In view of the extraordinary magnetic properties obtained by Cioffi² when the final traces of impurities are removed from iron by hydrogen treatment just under the melting point this material was subjected to a similar treatment. Through the cooperation of Dr. S. Dushman, at the General Electric Laboratories, both the wire and the plates were heated in a stream of undried hydrogen for 72 hr. at temperatures between 1375° and 1420° C. This treatment was effective in reducing the oxygen from 0.01 to 0.002 per cent and carbon from 0.016 to 0.009 per cent, as shown in Table 1. During treatment at this high temperature, an undesirable contamination of the iron occurred, however. The manganese and phosphorus contents rose, the contamination apparently coming from the refractories that lined the furnace, although all physical contact of specimens and lining was avoided. Thus the purity of the iron, like that of all "pure" iron material, leaves something to be desired. It was the best obtainable. Some untreated iron was reserved for comparative tests. The chemical analyses throughout this work were carried out through the cooperation of Dr. Anson Hayes, of the American Rolling Mill Company.

The wires were 4 mm. thick; the plates 2 mm. and 6 mm. Bare wire, cleaned of all drawing compound, was used in most of the tests. In a few instances it was coated to produce a "shielded arc" such as has recently yielded commercially a weld metal of markedly superior properties. The coating contained cellulose with sodium silicate as a binder and some titanium oxide to reduce porosity and to stabilize the arc electrically. These rods were coated for us by the cooperation of the A. O. Smith Corporation. The iron plates were used to line a 90° V-groove between two steel plates each $\frac{1}{2}$ in. thick, the plates serving as "backing" to prevent the arc from melting through the thin iron lining and to diminish magnetic blowing of the arc.

The argon was obtained from the Incandescent Lamp Department of the General Electric Co. As received, the gas contained approximately 1 per cent nitrogen. Carbonaceous gases were below 30 parts per million. The argon was given final purification by a misch-metal discharge, and when analyzed before use showed a purity of 99.3 to 99.6 per cent. The first few seconds of welding raised this purity considerably, owing to the scavenging action of the iron vapor coming off in large volume from the welding arc. The composition of the steel welding wire used for comparisons is given in Table 1. The wire was contributed by the Page Steel and Wire Company.

All welding was done by an automatic machine¹, not by hand. Since no penetration was possible when welding in argon, multilayer welding was out of the question and single-layer welds were used. A layer was made as thick as possible by slow travel of the welding table. Nevertheless, specimens smaller in size than the standard had to be used. The tension specimens were $\frac{1}{4}$ in. in diameter at the ends, undercut to $\frac{3}{16}$ in. on the shank of the specimen. To obtain values for elongation that would be comparable to those obtained with the standard 0.505-in. round specimen, the formula $l = 4.5\sqrt{A}$ was used to compute the proper gage length. This computation gave a gage length of approximately 0.75 in. The welds made in air were multipass welds but the tension specimens were cut to the same size, nevertheless, so that all test results would be comparable.

THE WELDS

Chemical Compositions

Welds in Argon.—The compositions of the wires and welds are given in Table 1. The welds are not homogeneous chemical samples, but vary somewhat, especially those made in air. The individual values are given as footnotes to the table. When welding with iron in argon, perhaps the most significant change to be noted is the slight rise of oxygen content

TABLE 1.—*Compositions and Physical Properties of Wires and Welds*

	State- ment of Carbonyl Iron Manu- facturers, Per Cent	Hydro- gen- treated Carbonyl Iron, Per Cent	Iron De- posited in Argon on Iron Plate, Per Cent	Covered Iron De- posited in Air on Iron Plate, Per Cent	Iron De- posited in Argon on Steel Plate, Per Cent	Covered Iron De- posited in Air on Steel Plate	Iron De- posited in Air on Steel Plate	Steel Welding Wire E, No. 1 A, Per Cent	Steel De- posited in Argon on Steel Plate, Per Cent	Covered Steel De- posited in Air on Steel, Per Cent	Steel De- posited in Air on Steel Plate, Per Cent
C	0 016	0 009	0 007	0 022	0 005			0 046	0 014		0 025
Mn	0 000	0 026	0 006	0 005	0 006			0 11	0 120		0 091
P	0 000	0 010	0 004	0 025	0 004			0 006	0 006		0 006
S	0 000	0 005	0 004	0 004	0 005			0 021	0 027		0 023
Si	0 000	0 002	0 003	0 18	0 003			0 002	0 004		0 090
N:		0 002	0 006 ^b	0 017	0 098			0 003	0 015 ^c		0 172
O:	0 01	0 002	0 006	0 152 ^c	0 265 ^d			0 036	0 012		0 276 ^e
H:		0 0002	0 0008	0 0009	0 003			0 0004	0 0006		0 005

PHYSICAL PROPERTIES											
Ultimate strength, lb per sq in .	29,300	40,600	58,400	65,600	47,100	56,200	62,800				
Yield strength, lb per sq in		23,400	43,900	38,100	24,200	41,400	37,750				
Elongation, per cent in $\frac{3}{4}$ in	a	29 4	12	4	27	14	5				
Reduction of area, per cent	100 —	90	15	3 5	95	15	5				
									Too porous for test	64,900	60,100
										43,200	45,600
										23 3	10
										30	6 3

^a Plastic flow obliterated gage marks^b Nitrogen values include argon^c An average of two individual values 0 160 and 0 143^d An average of two individual values 0 259 and 0 270^e An average of two individual values 0 244 and 0 344

of the metal from 0.002 to 0.006 per cent. It indicates that the argon was not perfectly pure, in spite of the precautions exercised. The apparent rise of nitrogen when welding in argon from 0.002 to 0.006 for iron (and from 0.003 to 0.015 for steel) is probably apparent only. Since the vacuum fusion method used for chemical analysis does not differentiate between nitrogen and argon probably most of the gas reported as nitrogen in the argon welds was argon. Separate determination of nitrogen by the Allen method is under way but not yet completed. A substantial loss of manganese and phosphorus from the iron appears to take place when welding in argon. In this relatively pure inert gas, it seems that impurity elimination from the electrode wire may be a matter of differential evaporation rather than oxidation, although a little oxygen is present. Hydrogen rises from 0.0002 to 0.0008.

The steel welds in argon, aside from the "argon" pickup, show a reduction from 0.036 oxygen in the wire down to 0.012 per cent in the weld, and a substantial reduction in carbon (0.046 to 0.014). This reduction probably occurs as a CO evolution. The porosity of these welds, shown in Figs. 2 and 3, may be attributed to this gas evolution.

Welds in Air.—The pure-iron welds in air differ little in composition from those in argon except for the high gas content of the air welds. Nitrogen is 0.098, oxygen 0.265, and hydrogen 0.003 per cent, all very high indeed. The steel welds in air are characterized by an even higher gas content: 0.172 nitrogen, 0.276 oxygen, and 0.005 hydrogen. For some reason, the silicon is up also. The hydrogen probably comes from decomposed atmospheric water vapor.

Covered Welds in Air.—The covered-iron welds are in general intermediate with respect to those made in argon and those made in air. Nitrogen is excluded by the coating better than oxygen. Thus nitrogen is 0.006 in argon, 0.017 in covered-wire welds, and 0.098 in air, showing about 85 per cent exclusion. Oxygen, evidently from the coating, rises from 0.006 in argon to 0.152 in covered-wire welds and to 0.265 in air, showing only about 60 per cent exclusion by the covering. The covering raises the carbon, phosphorus and silicon in the welds, by chemical reduction of the coating. It appears to lower the manganese. Comparative figures for covered-steel welds are not yet available.

Macrostructure

In Argon.—A single-layer deposit of iron in argon is shown in Fig. 1. The sharp line of separation between weld and plate resulting from the absence of crater formation and penetration noted above is visible, although partly obscured in preparation of the specimen. This weld is entirely free from porosity. With drastically purified argon, the welds are entirely sound. When the purity drops, slight porosity is encountered

in the iron welds. Also, when the carbonyl iron wire (0.01 per cent oxygen) was used without hydrogen purification, the welds in purified argon were porous. This seems to indicate that the presence of very little oxygen, either in the wire or in the atmosphere of the arc, will result in porosity.

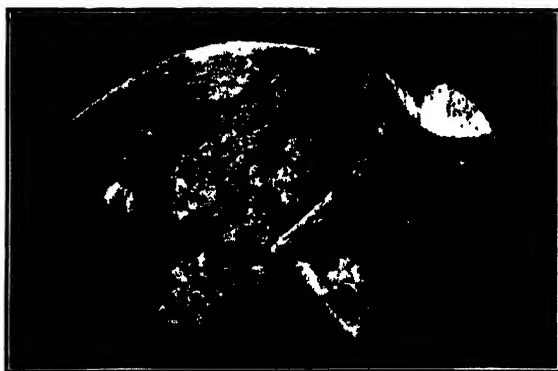


FIG. 1.—IRON WELD IN ARGON ON IRON PLATES. $\times 3$.

In order to investigate thoroughly the lack of penetration observed in argon welds, a considerable number of experiments were carried out using



FIG. 2.—STEEL WELD IN ARGON ON STEEL PLATES. $\times 3$.

the cheaper steel wire and plates. The analysis of the steel is given in Table 1. Every combination of arc length, current, welding speed and wire manipulation conceived of was tried without once obtaining effective penetration; that is, crater formation. Fig. 2 shows a multilayer weld of this kind, the section being taken near the beginning of the layer.

Owing to the slight degree of impurity of the argon at the beginning of the weld, slight penetration is shown in the lowest layer, but upon completion of almost every weld of this kind the connection of weld to plate was so limited that the entire weld could be lifted out of the groove with the fingers. The surfaces of each layer were silvery bright, with no indication of any slag or oxide layer to obstruct crater formation by the arc. Nevertheless, no crater formed. Fig. 3 shows a single-layer weld. It was lifted out of the V without difficulty, because of the absence of penetration.

Gas cavities are numerous in these welds and it will be noted that the contours of these cavities are smoothly rounded. Changing the welding

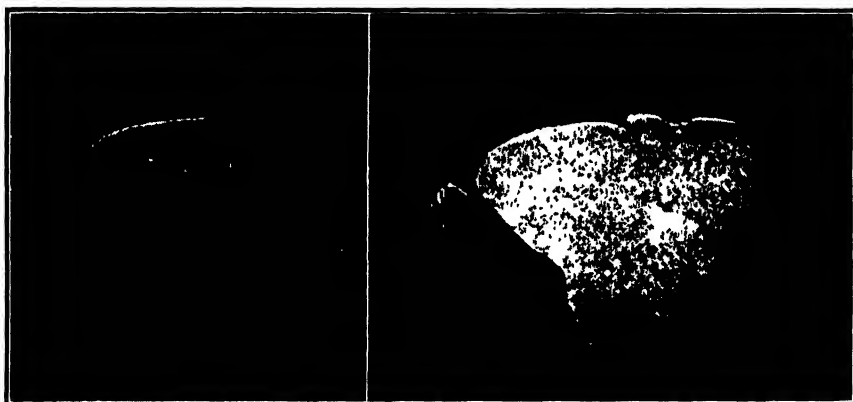


FIG. 3.

FIG. 4.

FIG. 3.—STEEL WELD IN ARGON ON STEEL PLATES. $\times 3$.FIG. 4.—IRON WELD IN AIR ON IRON PLATES. $\times 3$.

current within the entire range from 60 to 180 amp. was ineffective in eliminating porosity. In an attempt to keep the weld metal molten long enough to permit escape of the gases that caused this porosity, very thin sheets of base metal were used instead of the thicker plates, but without success. Because of this prevalent porosity, no physical tests of these welds were made.

In Air.—When air replaces argon, the iron welds reveal the ordinary crater formation and ordinary penetration as shown in Fig. 4. The gas cavities are somewhat more angular. Such cavities probably would be far more effective as "stress raisers" than the smooth ones found in argon welds, and would show lower strengths. The structure of steel welds in air is quite familiar and is not shown here.

Interest in the lack of crater formation in argon led to trying various admixtures of air with the argon. A mixture of 50 per cent argon, 50 per cent air gives about the same penetration as does air. With 90 per cent argon, 10 per cent air, a substantial penetration can still be noticed

(Fig. 5). There was a shallow crater at the end of the layer, indicating that very little air is necessary for crater formation. The cavities are predominantly angular.

Covered Wires.—When a cellulose-base coating covers the iron wire, penetration is still not prevented (Fig. 6). Porosity seems, if anything, more pronounced than in the unshielded welds. The cavities are angular also. The macrostructure of welds of covered steel wire is not illustrated.

Microstructure

Iron.—Large-grained ferrite, apparently pure, is the characteristic microstructure of the iron in argon welds (Fig. 7). Annealing this metal at 600° C. in hydrogen for 7 hr. to break down supersaturation and



FIG. 5.

FIG. 6.

FIG. 5.—STEEL WELD IN 90 PER CENT ARGON AND 10 PER CENT AIR. $\times 3$

FIG. 6.—IRON WELD IN AIR ON IRON PLATES $\times 3$.

approach the equilibrium state produces very little change (Fig. 8) except in the veining of the ferrite. The grain size is perhaps slightly smaller, but not definitely so. It would be difficult to identify any of the impurities present, although analysis shows 0.007 carbon and 0.006 oxygen. The specimens were, of course, sectioned to avoid the surface effect of the hydrogen anneal, slight though it may be at this low temperature and for this short time.

When iron is welded in air, the case is quite different. In the as-welded condition the structure is one of quite small ferrite grains (Fig. 9) pretty well peppered with inclusions. The correlation of oxygen and nitrogen with grain size reminds one of the conditions usually found in open-hearth steel. After annealing (Fig. 10), the grain size is large, the "pepper" (probably oxide particles) is clearly visible and with it an abundance of nitride needles. This structure corresponds with the chemical composition of 0.098 per cent N_2 and 0.265 per cent O_2 .

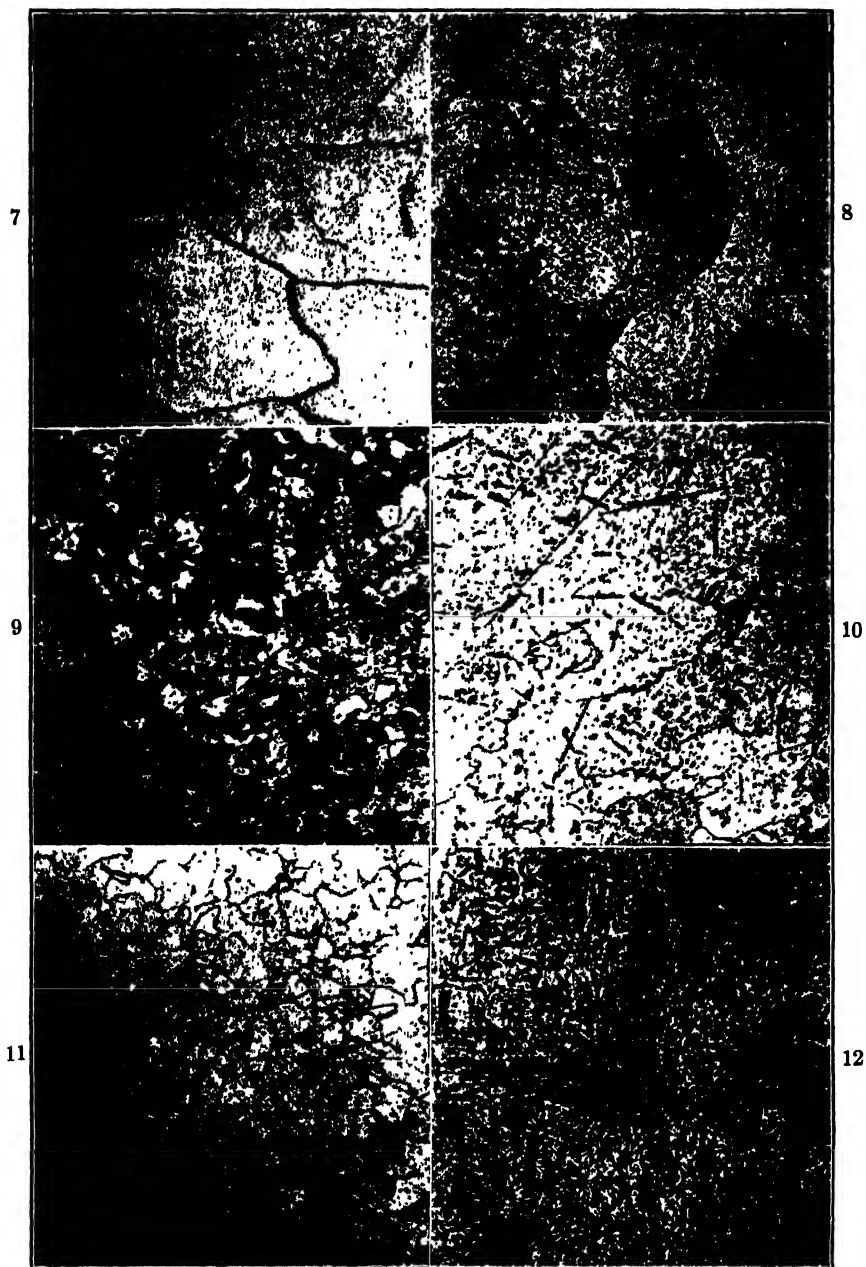


FIG. 7.—IRON WELD IN ARGON, AS WELDED. $\times 180$.

FIG. 8.—IRON WELD IN ARGON, ANNEALED AT 600°C . $\times 180$.

FIG. 9.—IRON WELD IN AIR, AS WELDED. $\times 180$.

FIG. 10.—IRON WELD IN AIR, ANNEALED AT 600°C . $\times 180$.

FIG. 11.—COVERED-IRON WELD IN AIR, AS WELDED. $\times 180$.

FIG. 12.—COVERED-IRON WELD IN AIR, ANNEALED AT 600°C . $\times 180$.

The cellulose-coated wires gave weld metal intermediate in grain size, "pepper" and nitride needles to that obtained in argon and that obtained in air, corresponding with the intermediate amounts of oxygen and nitrogen in the metal (Table 1). The structures of coated iron welds before and after annealing are shown in Figs. 11 and 12.



FIG. 13.—STEEL WELD IN ARGON, AS WELDED. $\times 180$.

FIG. 14.—STEEL WELD IN ARGON, ANNEALED AT 600°C . $\times 180$.

Steel.—When steel is welded in argon, large-grained ferrite, apparently pure, is again obtained (Fig. 13). The grains seem to have rougher, more acicular boundaries than those of pure iron. But when annealed (Fig. 14), this ferrite shows a considerable quantity of "pepper," which may be oxide particles ($\text{O}_2 = 0.012$ per cent) but practically no nitrogen ($\text{N}_2 + \text{A} = 0.015$ per cent), corresponding again to the chemical composition of the metal. The grain size is large, both before and after annealing. The microstructure of steel welds, both coated and uncoated, in air are

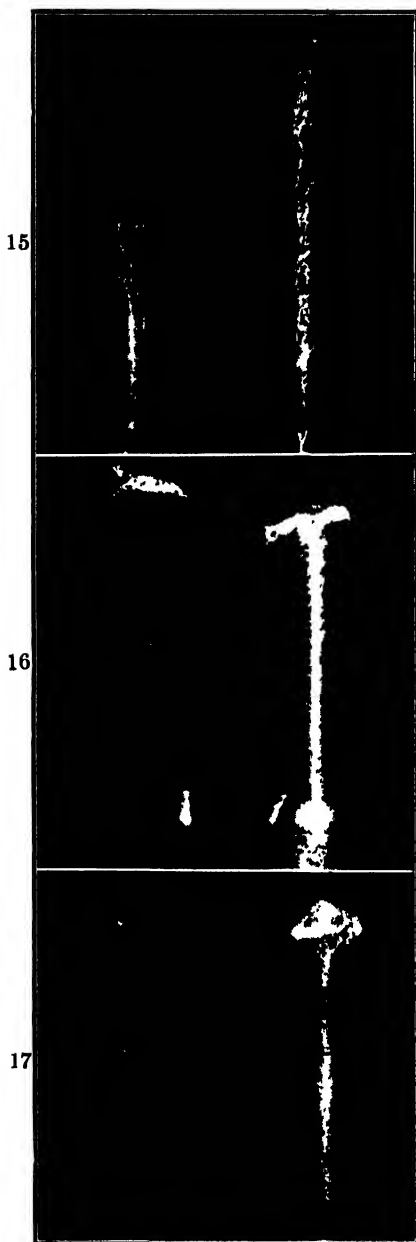
well known and are not reproduced here. In general, the microstructures correspond with that indicated by the chemical compositions.

Strength

Iron Welds.—The strength of the pure-iron welds in argon is very low and is in conformity with their high purity and coarse grain size. Thus, 23,400 is the yield point and 40,600 lb. per sq. in. is the tensile strength (Table 1).

The strength data of Duftschmid, Schlecht and Schubardt⁴ for carbonyl iron are: ultimate strength, 28,000 to 40,000 lb. per sq. in.; yield point, 15,000 to 24,000. Annealed electrolytic iron⁵ averages 40,000 to 55,000 ultimate strength and 20,000 to 25,000 yield point, while vacuum-fused and annealed electrolytic iron shows 35,000 to 40,000 tensile strength with 10,000 to 20,000 yield point. The strength of hydrogen-treated carbonyl iron, before welding, that is, 29,800 (Table 1) corresponds to the low region of the German values 28,000 to 40,000. The welds of this iron in argon, however, are much stronger; i.e., 40,600 and 47,100. Some of the increase no doubt is attributable to the slight oxygen pickup in argon, some to rapid quenching and some to grain-size difference.

If these welds are made in air instead of in argon, the yield point is raised from 23,400 up to 38,100, and the tensile strength is raised from 40,600 up to 65,600 lb. per sq. in., again giving a clear revelation of the important influence of ordinary air during welding upon the properties of the weld metal. It



FIGS. 15-17.—FRACTURED TENSION SPECIMENS. $\times 3$.

Fig. 15.—Iron weld in argon.

Fig. 16.—Iron weld in air.

Fig. 17.—Covered-iron weld in air.

seems clear that when made in air the strength of mild-steel welds, like those of pure iron may also be due primarily to the action of the oxygen and nitrogen absorbed by the metal, and only secondarily to the chemical composition of the wires.

Of the greatly increased strength of iron welds in air (38,100 yield point; 65,600 ultimate strength) over those in argon (23,400 and 40,600) a part may be attributed to grain size. The argon welds have an average grain size of 29 grains per square millimeter; the air welds, 385 grains per sq. mm. This finer grain size might account for as much as 4000 or 5000 lb. per sq. in.⁵ of the total rise of 25,000.

When the pure-iron wire was deposited upon mild-steel plates (0.17 per cent C), the results, both in argon and in air, were not essentially different from those obtained above with pure-iron plates. Naturally, since no craters form in argon, there was practically no penetration of the arc into the steel plates and little or no contamination of the weld by the plate stock was possible. For these results, see Table 1.

The coated-iron weld has risen in tensile strength from 40,600 for argon up to 58,400. The grain size is 230 grains per sq. mm. Owing to contamination of the weld by the coating, several elements are greater in amount in the weld than in the wire. The yield point of the covered-iron weld (43,900) is actually higher than that of the iron weld in air (38,100). Also, it is higher than that of the covered-*steel* weld in air (43,200), noted below. Too much emphasis cannot be laid upon the exact quantities denoted by these figures, however, for, as noted above, the welds are not entirely uniform in character and averages of a large number of specimens were not available.

Steel Welds.—When steel welds were attempted in argon, the weld metal obtained was so porous (Figs. 2 and 3 and noted above under Macrostructure) that it made tests uncertain in meaning; hence none are reported.

In ordinary air, the steel welds show the usual strength values; namely, about 60,000 lb. per sq. in. tensile strength and 45,000 yield strength. The steel welds were made from electrodes containing 0.046 per cent C and 0.11 per cent Mn, and after welding 0.172 N₂ and 0.276 O₂. It would seem that these welds should be much stronger than the iron welds, but actually they are not as strong. The strength of the covered-steel welds (64,900) is above that in air (60,100), probably because of pickup from the coating. The yield point is slightly lower.

Plasticity

Iron.—The plasticity of iron welds in argon—i.e., 30 per cent elongation and 90 per cent reduction—indicates what is achievable when air is excluded. When the iron is welded in air the plasticity drops to 4 per cent and 3.5 per cent, showing the amazingly strong effect of gases in the

weld on the plasticity. When the iron is coated, these values rise only part way to the high plasticity obtained by the extensive protection of an argon atmosphere. They rise to 12 and 15 per cent.

Steel.—Comparing the plasticity values for iron welds in air (4 and 3.5) with those of steel welds in air (10 and 6.3), it is clear that the alloys in the steel have exerted a beneficial effect on its plasticity. When the steel is given additional protection by coating, these values rise to 23.3 and 30 per cent. But when the pure iron is coated, its plasticity values rise, as noted above, only to 12 per cent elongation and 15 per cent reduction of area, just about one-half that of steel with the same coating. The proportionate rise for iron and for steel after coating is about the same, it is true, but the small amount of alloys in the steel seems to exert almost as great an effect in raising the plasticity values (from 4 and 3.5 for pure iron up to 10 and 6.3 for steel) as does the coating, which raises it again from 10 and 6.3 up to 23.3 and 30. This is quite conceivable. But why the coating should benefit steel welds so much more than it benefits pure iron welds is not at first entirely clear. The analysis of the coated-steel welds when available may indicate the reason for their superiority over welds of coated pure iron.

Figs. 15, 16 and 17 show the fractured tensile specimens. The roughened external surface of the pure iron specimen made in argon (Fig. 15) shows that the ductility of the metal is very high; also, the elongation takes place throughout the entire test length. The great reduction of area, 90 per cent (Table 1), is evident from the sharp point to which the bar is drawn at the point of fracture. Note in contrast the square end of the specimen welded in air (Fig. 16), which shows very little reduction of area (3.5 per cent) and very little elongation (4 per cent). The destruction of plasticity in the weld by the action of air during welding is clearly shown here. The covered-iron weld has a somewhat greater amount of ductility and reduction of area than that of the uncoated-wire welds, but the ultimate in shielding action seems by no means to be attained with the coating used in these tests. Specimens of steel welds are not shown.

Age-hardening of Weld Metal

The weld specimens were subjected to quench-aging treatments. Hardness readings also were taken on the metal in the as-welded condition as soon as possible after the specimen could be prepared, which was a maximum of 20 min. after welding was completed. In the quench-aging tests, specimens of the welds were heated to 525° C. in a lead bath and quenched in iced brine; hardness readings were taken at intervals after the treatment (Fig. 18 and Table 2). The curves show that no age-hardening was detected in pure-iron welds made in argon, but that the

welds made in air, both with the bare wire and the covered wire, age-harden substantially; owing, no doubt, principally to the nitrogen content.

TABLE 2.—*Complete Age-hardness Data*

Hardness after Welding		Hardness after Quenching	
Time Elapse	Hardness, Rockwell B	Time Elapse	Hardness, Rockwell B
IRON WELD IN ARGON			
19 min.	37-38-39	2 5 min	40-40 5
30 min.	36	7 5 min	40 39
1 5 hr.	37	12 5 min	41-38 5
7 5 hr.	38	17 5 min.	41
17 hr.	38 5	27 5 min	39 5
25 5 hr	37	47 5 min	40-41
96 hr.	37	3 hr	40
840 hr.	37	552 hr.	39-38 5
IRON IN AIR			
17 min.	80-79	4 min	64
71 hr.	82-80	7 min.	71
506 hr.	82	11 min.	79
792 hr.	84	27 min	84
		5 hr.	83
		30 hr.	85
		78 hr.	88 5-90
		245 hr.	92
COVERED IRON IN AIR			
19 min.	68	5 min.	60
1 25 hr.	68-71	10 min.	65
19 5 hr	76 5-76	25 min.	65
91 5 hr.	75 5-78	5 hr.	65-67
263 hr.	82-84	30 hr	71-69
698 hr.	80-82	78 hr	71
		270 hr	73

SUMMARY AND CONCLUSIONS

1. The impurities in the iron appear to be removed by *differential evaporation* in the arc in argon. Oxygen is not necessary for their removal.
2. The properties of the weld metal, especially its plasticity and formability, are changed profoundly by the action of the air upon the metal during welding. The oxygen and nitrogen contents of the metal rise sharply.
3. The metalloids (C, Mn, Si, etc.) in steel exert a protective action during welding in air and preserve a part of the formability of the metal.

4. Cellulose coating is partially effective in preserving the formability of pure iron welds in air. It is more effective on steel than on pure iron. But it is not fully protective even on steel.

5. Steel welds in argon are porous. Iron welds are not. All welds in argon lack "penetration" or crater formation.

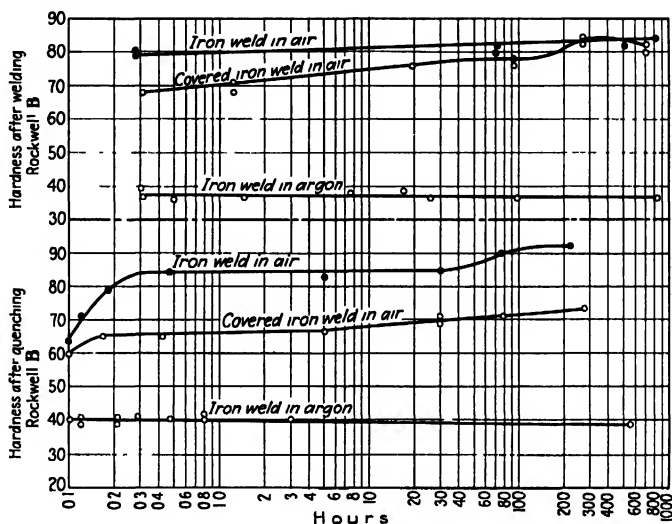


FIG 18 —AGING RESULTS

6. The grain size of iron welds seems to depend upon the oxygen content of the metal.

7. The iron welds in argon show no hardness increase following quench-aging.

ACKNOWLEDGMENT

For suggestions out of which grew the original program of this investigation, acknowledgment is due to Dr. S. L. Hoyt.

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DISCUSSION

(James L. Gregg presiding)

R. K. HOPKINS,* Jersey City, N. J. (written discussion).—The high degree of purity of welds made in argon with nearly pure electrode and base-metal material provides, as the authors point out, a base from which the effect of various elements in weld metal can be studied, and the authors are to be commended for the fundamental work which they have carried out.

The experience of Doan and Schulte in encountering lack of penetration when welding in an argon atmosphere is similar to that which the writer had a number of years ago when he attempted to weld in a near vacuum. The welds made with bare wire under this condition could be lifted out from the groove. In most cases the penetration was negligible.

The greater porosity reported for the coated carbonyl iron electrodes when welding upon base metal of the same material is undoubtedly due to the particular coating used.

The effects that have been attributed to oxygen and nitrogen are consistent with what is already known when these elements are present in irons and steels of lesser purity than the "pure" iron dealt with in this paper.

S. L. HOYT,† Milwaukee, Wis.—The oxygen content of the weld metal from the coated *pure iron* electrode deposited in the air is rather high. When that oxygen is determined as total oxygen, as here, it appears as so much oxygen, but by the fractional oxygen method it would presumably be found to occur as SiO_2 . This amount of silica would be dissolved from the coating by the metal of the weld rod. Furthermore, comparing the silicon content of the weld metal with this amount of silica, under the above assumption, shows that most of the silicon is oxidized. The oxygen of the metal from the bare, pure iron electrode would be returned as nearly all iron oxide, FeO , by the fractional oxygen method, since there is no silicon present. In view of this fact, the behavior of the coated *steel* rod is different, in that more silicon is produced in the weld deposit. I believe this may be due to a difference between the iron and the steel weld rod according to which the carbon of the steel rod helps reduce the silica of the coating. The results reported today tend to bear this out, because with no carbon in the pure iron rod, the authors presumably got less reduction of silica, though the dissolving action did occur.

S. DEPOY,‡ Dayton, Ohio.—I have found out in my experience that craters weaken the weld. For small work I get greater durability and strength when using straight polarity with bare wire. This eliminates craters in the parent metal. I understood the authors to say that it was desirable to have a crater. I do not know what the explanation of that would be.

When using covered wire, the reversed polarity caused me to get a vesicular structure in the weld and weakened the weld. Some wires will not do it and others will. The human equation does not enter into that. I tried out all my men, and certain wires got that vesicular structure. I think I have obtained the best results when I did not get a crater.

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‡ Foreman of Heat-treating and Welding, Delco Products Division of General Motors Corporation.

J. J. CROWE,* Jersey City, N. J.—Why is there grain-size refinement in the pure iron specimens on annealing at a temperature well below the accepted critical range? The grain size in Fig. 8 after annealing at 600°C. is very much smaller than is Fig. 7, taken of the same material before annealing.

G. E. DOAN (written discussion).—We are in agreement with Mr. Hopkins that the porosity of the coated iron welds does not represent the best results obtainable with coatings. We used as simple a cellulose coating as possible in order not to complicate the interpretation of the results.

Dr. Hoyt wishes us to assume that all the oxygen in the coated pure iron weld is combined as SiO_2 . Calculation shows that there is enough silicon in the weld for this purpose and some in excess. Dr. Hoyt's rich experience in this field lends importance to this view. In the bare, pure iron weld, only about half of the 0.006 per cent oxygen could be so combined with silicon. But as we have seen today, the absolute accuracy of oxygen determination renders it unwise to attach too much importance to such small quantities as 0.003 per cent.

Dr. Hoyt concludes, logically, that the coating is more effective in preserving plasticity in steel than in pure iron, because of the additional protection against oxidation contributed by the carbon and other reducers in the steel. The chemical analysis of the coated steel welds is being made, and when finished will throw additional light on this question.

Mr. DePoy dislikes craters in welding, and I must agree that deep craters accompanied by undercutting, or craters left open at the end of a seam, are highly undesirable. Some penetration, however, through the surface film on the metal is quite necessary to insure a weld. In the argon welds, liquid metal merely deposits on unmelted plate and a weld is not secured.

As Mr. Crowe says, the grain size of the pure iron weld appears somewhat smaller in the specimen that has been annealed at 600°C.—below the transformation temperature of pure iron, which is about 915°C. Perhaps the veining of the annealed ferrite grains is somewhat deceptive in estimating the grain size of these specimens, for in general we found little difference between the two structures in this respect.

W. C. SCHULTE (written discussion).—One point we wish to make clear, we do not want to leave the impression that the coatings used on the pure iron electrodes are the best that can be produced. In asking the A. O. Smith Corporation to coat these rods, we stipulated a number of things that we did not want added, such as manganese, silicon and other metallic deoxidizers. The fact that the oxygen and nitrogen contents in the pure iron weld metals made in air are higher than those of commercial steels can also be explained by the fact that we had to rely entirely on the deoxidizing power of the coating, since we had no manganese, silicon or carbon present in the welding electrode.

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New Method for Welding Together Ferrous Metals by Application of Heat and Pressure

BY LEONARD C. GRIMSHAW,* MEMBER A.I.M.E.

(New York Meeting, February, 1936)

THE idea of bonding two dissimilar ferrous metals, and making use of both, is an old one. Tips have been brazed onto tool shanks for many years. The bonding of larger pieces to form whole bars and sheets has also been accomplished, but has received little attention in the technical literature, although a number of patents have been issued covering various methods for its accomplishment.

There are three main motives behind the manufacture of composite steels. One is that the physical properties of one steel may supplement those of another; a useful, but at the same time, hard, brittle steel may be backed by a soft ductile one, or a stainless steel may be backed by a steel possessing greater strength. Another motive is direct lowering of cost; an expensive steel may be backed by a less expensive one, bringing down the cost of the piece as a whole. The third motive is an indirect lowering of cost, as when a useful steel is backed by a steel that is easier to machine, so that machining cost on a finished product is lowered considerably. Often more than one of these motives lead to a decision to use a composite steel.

PREVIOUS METHODS

There are two methods in use that result in tolerably good bonds between ferrous metals: (1) the casting method, and (2) what we shall call the "heat-pressure" method. This "heat-pressure" method covers processes in which the bond is made between two prepared surfaces by heating them and then applying pressure. Usually sufficient pressure must be used to produce appreciable spread and elongation, or else we are merely brazing and not truly welding.

Casting methods for welding together ferrous metals have been used more than 74 years, and are described in the technical literature as applied

Manuscript received at the office of the Institute Nov. 14, 1935.

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to the making of such products as field frames for dynamos¹, armor plate², and casting steel on a forged hub³. A summary of most methods used until 1921 is given by Longmuir⁴, who speaks of the dearth of technical literature and research upon this subject. There are several later references to casting methods⁵⁻¹³.

"Copper-clad" and "nickel-clad" are methods of bonding steel to copper and nickel respectively, and do not come under the subject of combined ferrous metals.

In 1931 announcements appeared in several magazines and trade journals of a method for the "heat-pressure" welding of ferrous metals, the product being named "Plykrome," or "SuVeneer." No details of its manufacture were published. For details of heat-pressure methods of welding we must turn to the various patents. Summaries of the principal patents are given in a recent paper by Rogers¹⁴ describing a new method developed by P. A. E. Armstrong¹⁵, by which sheets, bars and shapes are welded together so that one metal really diffuses into the other. It is the purpose of the present paper to describe in considerable detail the commercial uses and applications of this new heat-pressure method of welding.

DIFFICULTIES IN PRODUCING A GOOD WELD

In attempts to produce metals welded together, whether by casting or by the application of heat and pressure, the finished product has not been perfect. Usually nonmetallic inclusions, or the introduction of a soft weak metal between the two metals it is intended to weld, prevent the formation of a strong bond. Physical distortion, or heat-treatment when the metals have different coefficients of expansion, usually result in rupture of the bond. For certain uses such bonds have proved commercially acceptable, but there is a much wider field open to metals really welded and diffused together so that the weld is as strong as the metals themselves.

Iron can be welded to iron, despite oxide or scale, by heating to a good red heat and applying pressure. The weld relies upon the fact that the pressure will elongate the two pieces of iron, breaking up the scale into small islands. The bond takes place between the areas of oxide-free iron surrounding these oxide islands.

Upon exposure to the atmosphere many alloy steels form an invisible film of what is probably oxide, but which behaves very differently from the heat oxide, or scale, upon ordinary iron. Whether this invisible film is a true oxide or not is outside the scope of this paper, but it will hereafter be referred to as an oxide film, because much reliable recent research supports this view. This invisible oxide film on alloy steels completely prevents any real bond from taking place when heat-pressure welding is

attempted. Even visibly clean pieces of alloy steel, protected during heating from all scale formation, are prevented from welding under pressure by this invisible oxide.

NEW METHOD FOR PRODUCING WELD

In the Armstrong method, the alloy steel is first given an electrolytic coating of pure iron. If the electrolytic iron is properly deposited upon the alloy steel, it will bond there, by diffusion, upon the application of



FIG. 1.—GENERAL VIEW OF IRON-PLATING PLANT.

heat alone. This pure electrolytic iron, with the alloy steel behind it, can then be welded easily by heat and pressure to any other piece of iron, or to another piece of alloy steel that has been given a similar coating of electrolytic iron.

Iron has been electroplated upon iron and steel to build up worn parts, particularly during the war. Often this iron was plated upon an intervening layer of copper, presumably to insure adherence of the electrodeposited iron to the worn part. Iron plating is used for the manufacture of electrolytic iron, the plating being stripped off the cathode after deposition. Sometimes the iron plating is purposely made extremely brittle, so that it may be removed from the cathode and pulverized. The Armstrong method of electrodepositing iron upon alloy steels employs a special technic that causes the iron plating to adhere to the base metal, and to make a permanent bond by diffusion when heated to a red heat, preferably about 1700° F. (927° C.) or more, without the application of pressure.

The Iron-plating Plant.—An Armstrong process iron-plating plant that has been in commercial use for nearly a year includes tanks for cleaning,

pickling, plating, washing, etc., and equipment for assembling the plated steel into composite billets ready for forging and rolling. General views of the plant are shown in Figs. 1 and 2.



FIG. 2.—IRON-PLATING TANK, WITH FILTER AND SUMP TANKS IN BACKGROUND.

The tanks are 8 ft. deep (going below floor level), 7 ft. long, and 5 ft. wide, so that fairly large billets and slabs can be handled. Fig. 3 is a sketch of the tank used for plating, showing the position of the iron plates used for anodes, and the manner in which the work is suspended by hooks from the cathode bar. Small pieces to be plated are held in specially constructed racks (not shown), that likewise are suspended from the cathode bar.

All tanks and piping holding corrosive liquids are made of iron lined with hard rubber, and the circulating pump and valves on the plating tank are made of durochlor. In the pickling tanks, the center bar from which the work is suspended is made the anode; in the plating and cleaning tanks it is the cathode. Direct current is supplied at between 4 and 6 volts. The plant is capable of handling between 6000 and 9000 lb. of billets of average size every eight hours.

Method Used for Iron Plating.—A step by step description of the operations performed on a single billet of alloy steel as it goes through the plating process will give a good idea of just how the work is handled in the plating plant.

The faces of the billet that are to make contact for subsequent heat-pressure welding should be reasonably flat. Scale will be removed during the electrolytic pickling, but time is saved by sand-blasting forged billets of high-speed steel containing cobalt, since this scale is exceptionally difficult to remove by pickling, and the billet will invariably become pitted before all the scale is off. The electrolytic pickling removes scale with ease from all other steels.

First the billet is cleansed of all grease by making it cathodic for a few minutes, at a low current density, in a tank of dilute sodium hydroxide that is heated to over 120° F. (50° C.) It is then transferred to a pickling

tank of 8N hydrochloric acid, where it is made anodic for about 15 min. at a current density of about 100 amp. per sq. ft. This length of time is sufficient to remove the scale from almost any billet except the high-speed steels containing cobalt.

This strong hydrochloric acid bath, operated electrolytically, seems to have a very long life indeed. Whereas such a bath used without the electric current would soon have built up an iron concentration high enough to render it useless for commercial pickling, the bath works electrolytically over long periods of time. Since this tank is lined with

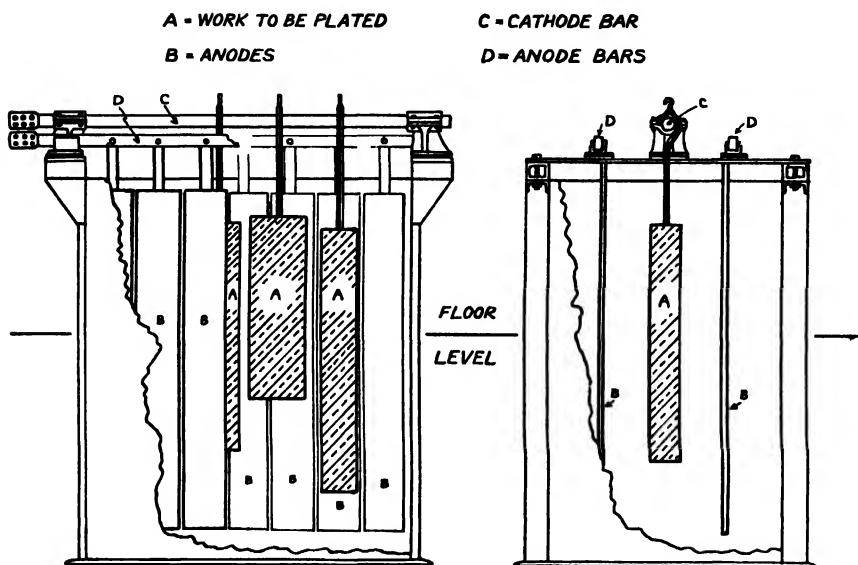


FIG. 3.—DIAGRAMMATIC SKETCH OF PLATING TANK.

hard rubber, iron plates are suspended in the acid as cathodes. These plates are seldom removed; the iron content of the acid is so high that the plates dissolve very slowly.

After this 15-min. anodic pickle the billet is removed, and washed and scrubbed free from sludge. All steels except those containing more than 3 per cent tungsten are now visibly clean and "shiny bright," but after exposure to the air during scrubbing are covered with an invisible oxide film, which is removed by a dip for 30 sec. in the hydrochloric acid solution. The billet, *while wet with the acid*, is immediately transferred to the plating bath and made cathodic.

Steels containing more than 3 per cent tungsten are covered with a black deposit (probably tungstides), which cannot be scrubbed off after the anodic pickle in hydrochloric acid. After scrubbing, a tungsten-steel billet is further cleaned by treatment in a bath composed of 115 grams

per liter sodium hydroxide, and 15 grams per liter citric acid, in which the billet is made anodic for 15 min. at a current density of 25 amp. per sq. ft.¹⁶ Following this, a 30-sec. dip in the hydrochloric acid bath prepares the steel for electroplating, and it is transferred, *wet with acid*, to the iron-plating bath.

The iron-plating bath used is a Fisher-Langbein solution: 4N ferrous chloride, 6N calcium chloride, and 0.01N free hydrochloric acid. The bath is operated at a temperature higher than 180° F. (82° C.), the solution being circulated and completely filtered during every 20 min. The work is made cathodic, and plated at a current density of 100 amp. per sq. ft. or more. One hour's plating at 100 amp. per sq. ft. gives a



FIG. 4.—VISE USED IN ASSEMBLING COMPOSITE BILLETS.

deposit of iron 0.006 in. thick, which is sufficient for most alloy steels. The resulting plate is soft, ductile, smooth, and will not chip or spall off.

The billet is next washed and dried quickly, so as to be free from rust. It is now ready to be assembled into a composite billet.

Assembling of Composite Billets.—Iron will weld to iron by heat pressure, but here there is only a very thin electrolytically deposited layer of iron, free from rust, and unless precautions are taken it will all scale away while the billet is being brought up to forging temperature. It is desired also to get a weld entirely free from oxide—free, that is to say, from little islands of scale oxide—because wherever this oxide exists there will be no weld; a weld will only be made between the oxide islands after elongation of the composite billet.

The two or more pieces that go to make up a composite billet are assembled in various ways, depending upon the position and amount of the alloy steel required in the finished product, but each component

piece is pressed firmly against its neighbor in a vise provided with powerful jacks (see Fig. 4) and then welded together by electric arc. It must here be stressed that this electric arc welding has no part in the heat-pressure welding to take place in the composite billet, other than to hold the pieces together and prevent scaling away of the electrolytic iron while the composite billet is being heated for forging or rolling. The electric arc weld will always be ground away before finish rolling, except on plates from which trimming of the finished product will remove it.

Stainless steels can be assembled easily by electric arc welding into any form of composite billet, but high-speed steels offer a few difficulties. Being air-hardening, precautions must be taken to prevent cracking of the high-speed steel alongside the electric arc weld. On larger pieces this trouble can be overcome most readily by using double (or two-high) assemblies, so that no electric arc welding need be done on the high-speed steel itself. Fig. 5 shows such an assembly, strapped together at the sides with strip $\frac{3}{16}$ in. thick, with separating material between the two pieces of high-speed steel. This composite billet is heat-pressure-welded, then the straps are chipped off with a pneumatic chisel (for they do not weld to the assembly) and the whole next separated into two halves. Separation into halves is easy because of the separating material put between the two pieces of high-speed steel. If precautions could conveniently be taken to plate only one face of each piece of high-speed steel, no separating material would be necessary. It is optional whether we use one of the special stop-off lacquers that are on the market, to prevent deposition of iron, or plate the whole piece and then use a separating material in order to prevent welding in this assembly, but we favor the use of a separating material because it is less expensive.

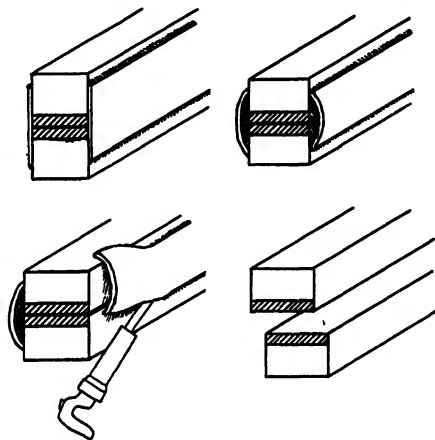


FIG. 5.—TWO-HIGH COMPOSITE ASSEMBLY.

Thickness of Iron Plating Required.—An electrolytic iron coating 0.006 in. thick, when protected against scaling during heating by electric arc welding of the composite billet, is sufficient for most alloy steels, but has to be twice as thick on high-speed steels containing cobalt. These steels possess such great powers of diffusion into the electrolytic iron that while the billet is being brought up to forging temperature the tungsten and cobalt in the steel will diffuse entirely through an electrolytic iron coating 0.006 in. thick, and unless the coating is thicker, by the time the

billet is ready to forge we would be attempting to weld by heat and pressure not iron to iron but iron to a tungsten-cobalt alloy of iron, which cannot be done.

Forging and Rolling.—Forging or rolling of the composite billet produces a perfect weld. The temperature used is that demanded by the steel in the assembly that requires the highest temperature for good hot-working qualities. Warping and twisting of the composite billet due to unequal coefficients of expansion are always encountered once the perfect weld has been made, and must be overcome either by using double assemblies such as shown in Fig. 5, or by the use of special guides. Where there is a great difference in hot-work ductility between the components, special rolls and guides must be made to guard against flow of the more ductile metal around the less ductile one.

Sheets rolled on a plate mill are free from both these troubles if the sheets are assembled and rolled two-high. Normal trimming of the sheet removes all material that may flow up around the edges.

It is worthy of notice that where a perfect weld is produced a steel such as high-speed steel will elongate during rolling almost as much as the softer backing material. The roll pressure on the bar as it passes through the rolls is vertically downward, and if the weld is perfect, so that there can be no slip, the two kinds of steel must elongate together. Sideways spread of the softer steel is a different problem, and is overcome only by special grooves in the rolls.

BILLETS AND FINISHED MATERIAL

Fig. 6 illustrates some of the shapes and positions of insert that can be produced in finished material, and the composite billet necessary at the start. On small squares that receive one oval pass during finish rolling, the insert is moved from the flat side over into the corner of the bar, so that it is not necessary to start with a corner insert billet except on large sizes that do not get an oval pass. The omission of an oval pass, or the putting in of two oval passes instead of one, results in the insert remaining across the flat side (bar *C*, Fig. 6).

The billet for bar *G* (Fig. 6) can be made in two ways. In one, a round bar that need not be a very tight fit is placed inside an alloy steel tube that has been plated on the inside with electrolytic iron, and the assembly electric-arc-welded to close up the ends. This method involves the drawback that if the tube is long, a special anode must be set up in the plating tank that will be inside the tube and yet not touching it. The plating bath possesses exceptionally good throwing power: it will plate the inside of a hole that is $2\frac{1}{4}$ in. in diameter and 10 in. long, but it is not good enough to plate properly the inside of a tube several feet long, even if the diameter is 6 in. The ratio between inside diameter

and length of piece that can be successfully plated has not yet been thoroughly investigated.

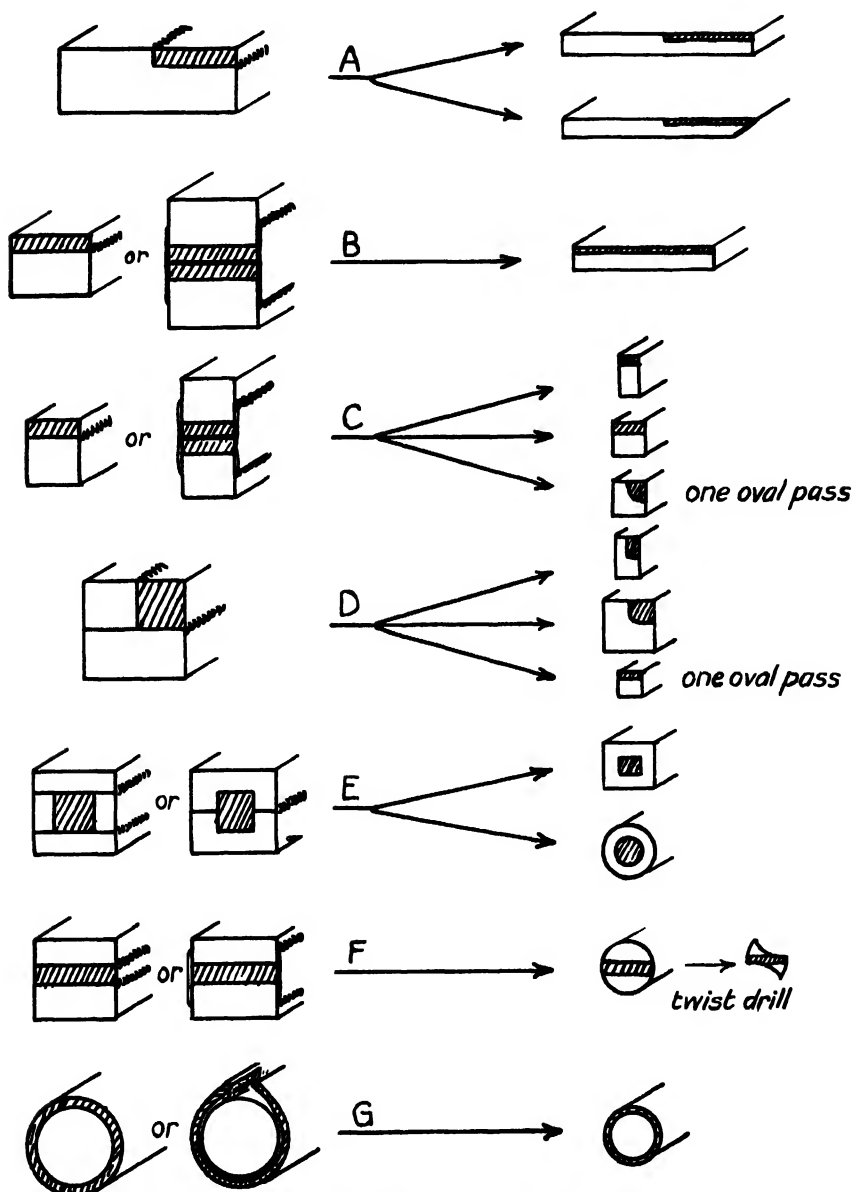


FIG. 6.—BILLET ASSEMBLIES USED FOR VARIOUS FINISHED COMPOSITE STEELS.

The other way to make the billet is to plate one side of a flat sheet, and then bend it in a press so that it can be electric-arc-welded with alloy-steel electrodes, in the form of a tube around the center bar.

In the plating of stainless steel, precautions should be taken to prevent iron from plating on the face of the stainless that is to become the useful surface of the finished product, because although nearly all the electrolytic iron will scale off during heating and rolling, the smallest particles remaining would impair the stainless properties. Also, diffusion of chromium into the electrolytic iron would reduce the chromium content of the surface. Grinding of the finished bar would remove these causes of trouble, of course. A good grade of black paint, chosen because it contains nothing that will harm the plating solution, will withstand the pickling and the hot plating solution sufficiently well to prevent the iron from adhering to the stainless steel. Paint and deposited iron can all be removed afterwards by light scrubbing, as it tends to peel off.

Sheets or plates clad with stainless steel have been rolled successfully from "two-high" composite slab assemblies, which leave the stainless free to move independently of the backing slabs during heating for rolling. By this means trouble due to the differences of expansion between the facing and backing materials before the weld is made by rolling is overcome. When attempted as a single high job, the greater coefficient of expansion of the stainless steel causes it to tear loose the electric arc welds that hold it to the slab of backing steel while it is being heated for rolling.

In making one of these special two-high composite slab assemblies, two stainless plates are separated by a mixture of aluminum oxide and silicate of soda, applied as a paste and then dehydrated. This mixture prevents the plates from welding or sticking together. They are electric-arc-welded entirely around their edges, so that they form a single watertight piece. In this form they are pickled and given a plating of electrolytic iron, then sandwiched between two slabs of backing steel cleaned by sand blast. These backing slabs are longer and wider than the stainless by several inches, depending upon the size of the assembly. With the stainless centrally located in the sandwich, the surrounding gap between the backing slabs is filled in and electric-arc-welded in such a way that the stainless has room to expand freely inside, while being protected from oxidation during heating for rolling. After rolling, the edges are trimmed off, and the separating material between the two pieces of stainless allows the two finished composite sheets to be pulled apart.

Finished composite sheets or plates prepared by this method may be of any thickness the plate mill can roll. Great reduction is not necessary to produce this weld: a good heat and a little reduction and the weld is made. Later heating strengthens the weld by diffusion. There is a wide field open for clad plates that are 2 in. thick, or more, as it is clearly in such heavy sections that important savings in cost of material are made.

The welds produced by this method are free from oxide inclusions, and show remarkable diffusion if the steel is reheated for forging, annealed, hardened, or otherwise raised to a bright red heat after the weld has once

been made. The mention of heat-treatment after welding reminds us that in choosing the components of a composite bar any heat-treatment that the finished bar may receive must be borne in mind. If one component is high-speed steel, for instance, the other component must be chosen to withstand the hardening temperature of high-speed steel. We have found two steels, one a medium-carbon manganese-molybdenum and the other a medium-carbon chromium-tungsten-vanadium steel, that are quite tough and undamaged after being given the hardening and drawing treatment of high-speed steels. Tools made of such composite pieces are much tougher than hardened high-speed steel, will withstand considerable shock, and can be bent appreciably before they will break.

Stainless sheets clad with ordinary 18-8 present the same difficulty as the high-speed steel, in that the backing material is not left in good physical condition after the clad sheet has been heated to 2100° F. (1150° C.) for the purpose of annealing the 18-8. However, there are 18-8 materials that do not require such high temperature: 18-8 containing high manganese and copper, known as Armstrong metal, need be annealed at only 1250° F. (680° C.); columbium-loaded 18-8 need be annealed at only 1700° to 1750° F. (925° C. to 955° C.); and none of these treatments impairs the physical properties of the backing steel.

In all clad products where there is a great difference of expansion between the two steels used, if the weld is not excellent heat-treatment will cause the sheet to burst or tear apart, often with explosive violence. All 18-8 clad sheets are of this kind and titanium-loaded 18-8 is particularly difficult to weld. The differences in expansion cause warping in all 18-8 sheets, but repeated heatings do not cause the weld to fail when made by the Armstrong process, and straightening does no damage.

QUALITY OF THE WELD

There are three important features of finished welds made by this method:

1. The weld zone is free from nonmetallic matter.
2. The weld zone can be heat-treated in the same way as an alloy steel.
3. The weld zone is strong and tough: a graduated alloy steel from the facing metal on the one side to the backing metal on the other side.

The photomicrographs in Figs. 8 to 18 are taken on a section ground at an angle of 45° to the plane of the weld. This has the effect of making the weld zone appear wider than if the photomicrograph were taken on a section ground at 90° to the plane of the weld, and shows more of the structure.

Fig. 7 shows the bond between 18-8 and a heavy deposit of electrolytic iron in a sample that was not subjected either to heat or to working. This bond is oxide free, although an etching stain along the junction between the two metals does not show this very well. This single photo-

micrograph of a cross section made at 90° to the plane of the bond is included to show how little can be seen and how misleading it may be. Fig. 8 shows much more of the bond. This is a piece of 18-8 upon which electrolytic iron was deposited, that was heated for 1 hr. at 1750° F. No inclusions are present, and diffusion has made a perfect weld; no forging

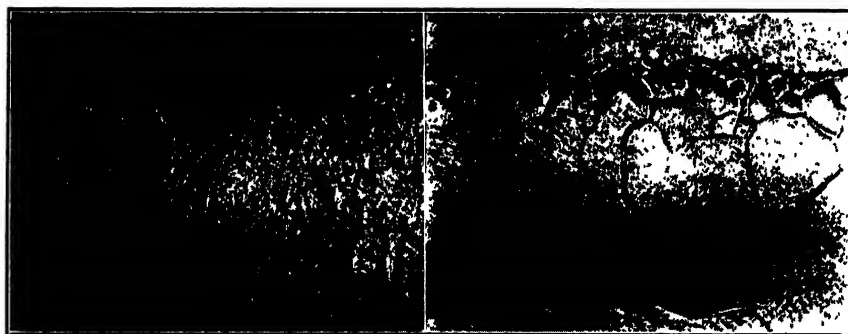


FIG. 7.

FIG. 8.

FIGS. 7 AND 8.—BOND BETWEEN 18-8 (TOP) AND ELECTRODEPOSITED IRON (BOTTOM).
X 750, REDUCED $\frac{1}{2}$ IN REPRODUCTION.

Fig. 7.—Section 90° through bond. Structure as deposited.

Fig. 8.—Section 45° through bond. Structure after diffusing 1 hr. at 1750° F.
Picric acid etch.

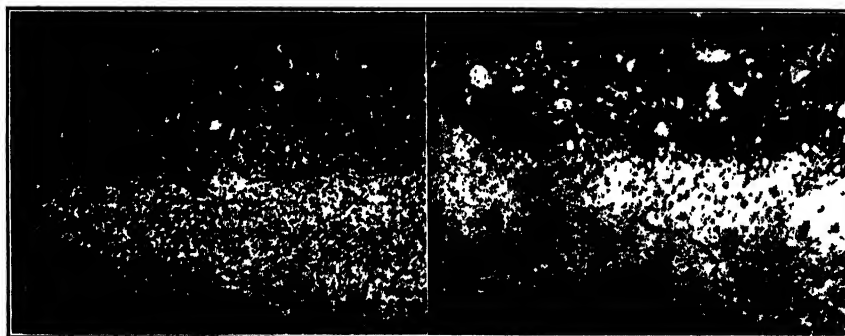


FIG. 9.

FIG. 10.

FIGS. 9 AND 10.—BOND BETWEEN HIGH-SPEED STEEL (TOP) AND ELECTRODEPOSITED IRON (BOTTOM). X 1000, REDUCED $\frac{1}{2}$ IN REPRODUCTION.

Fig. 9.—Section 45° through bond. Structure as deposited.

Fig. 10.—Section 45° through bond. Structure after diffusing 1 hr. at 1750° F.
Picric acid etch.

or rolling was done on this sample. A weld like this between the electrolytic iron and the alloy steel is made by diffusion while the composite billet is being brought up to forging temperature in the furnace.

Fig. 9 shows the bond between high-speed steel and electrolytic iron as deposited, and Fig. 10 shows the same after heating for 1 hr. at 1750° F. As in the 18-8, the weld is already made between electrolytic iron and high-speed steel before the heat-pressure weld is attempted between the

electrolytic iron and whatever other material is to become the backing steel.

Figs. 11 to 18 show completed welds between alloy steel and base material after forging or rolling.

Fig. 11 shows the weld, after annealing at 1675° F. between a 12 per cent cobalt high-speed steel and a backing material of 0.60 per cent carbon low-alloy steel, chosen for its toughness after the hardening and drawing treatment given to the high-speed steel. That the white zone between

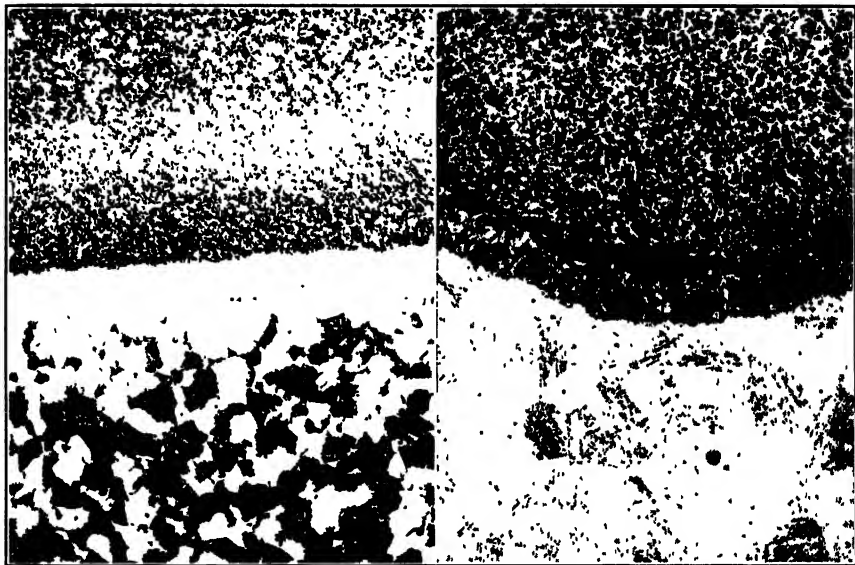


FIG. 11.

FIG. 12.

FIGS. 11 AND 12.—WELD BETWEEN HIGH-SPEED STEEL (TOP) WITH 12 PER CENT CO AND LOW-ALLOY STEEL WITH 0.60 PER CENT C (BOTTOM). DIFFUSION WELD ZONE IN CENTER. $\times 125$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Fig. 11.—Section 45° through weld. Annealed structure.

Fig. 12.—Section 45° through weld. Hardened and drawn structure. Picric acid etch.

the high-speed steel and the backing in this annealed sample is no longer electrolytic iron, but contains alloying elements picked up by diffusion, is best proved by Fig. 12, which shows the weld after hardening and drawing. Both photomicrographs were made from samples taken only a few inches apart on the same bar, and both were polished at a 45° angle to the plane of the weld. In such cases the annealed specimen invariably shows a comparatively wide white band of what was once electrolytic iron, which, after hardening and drawing, etches rapidly and apparently becomes narrower. It would seem as though part of this onetime electrolytic iron zone picks up alloying elements from the backing material, and part of it picks up elements from the high-speed steel, producing the effect of Fig. 12.

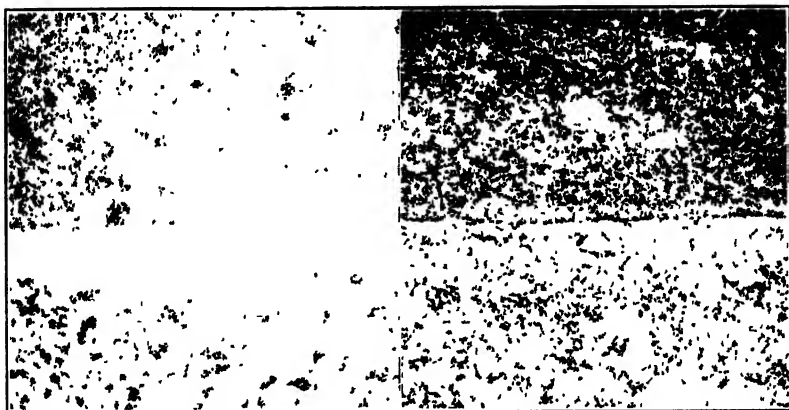


FIG. 13.

FIG. 14.

FIGS. 13 AND 14.—WELD BETWEEN KNIFE (1.20 PER CENT C-W-CR) STEEL (TOP) AND LOW-CARBON STEEL (BOTTOM). DIFFUSION WELD ZONE IN CENTER. $\times 125$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Fig. 13.—Section 45° through weld. Annealed structure.

Fig. 14.—Section 45° through weld. Hardened and drawn structure.
Picric acid etch.

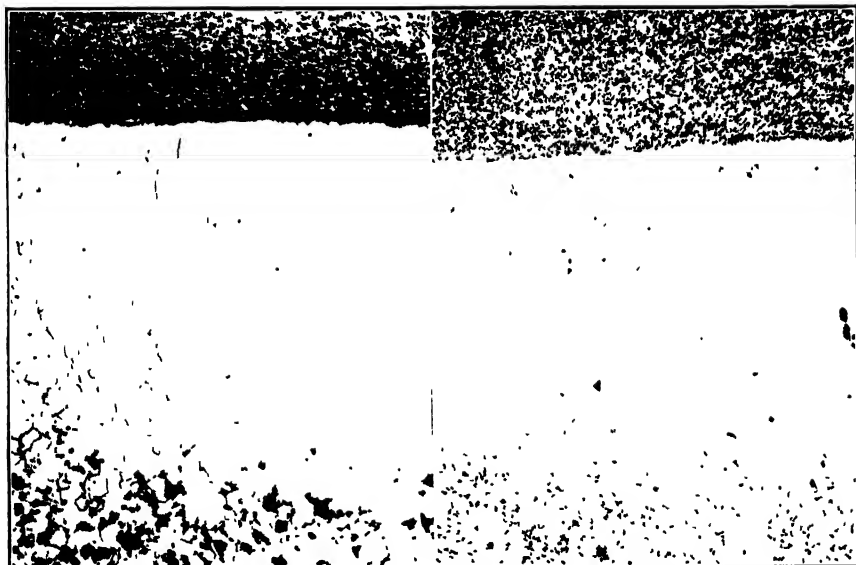


FIG. 15.

FIG. 16.

FIGS. 15 AND 16.—WELD BETWEEN DIE (1.6 PER CENT C, 12 PER CENT CR) STEEL (TOP) AND LOW-CARBON STEEL (BOTTOM). DIFFUSION WELD ZONE IN CENTER. $\times 125$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.

Fig. 15.—Section 45° through weld. Annealed structure.

Fig. 16.—Section 45° through weld. Hardened and drawn structure.
Picric acid etch.

Figs. 13 and 14 show respectively the annealed and the hardened and drawn structure of the weld between a knife steel (1.20 per cent C-W-Cr) and a low-carbon iron backing. Here again, after annealing there appears to be a zone of pure electrolytic iron, but after hardening and drawing this etches as an alloy material. Certainly it is an alloy material when it is annealed: the diffusion can hardly take place only upon hardening and drawing. In support of this, it must be remembered that after the weld is made by heat and pressure (first cogging) the steel receives one or two heatings for further rolling, and receives also the anneal



FIG. 17.

FIG. 18.

FIGS. 17 AND 18—WELD BETWEEN 18-8 (TOP) AND LOW-CARBON STEEL (BOTTOM).
DIFFUSION WELD ZONE IN CENTER.

Fig. 17.—Section 45° through weld. Etched with sodium cyanide then picric acid. Water quench from 2000° F. $\times 125$, reduced $\frac{1}{3}$ in reproduction.

Fig. 18.—Section 45° through weld. Picric acid etch. Structure after water quench from 2000° F. $\times 500$, reduced $\frac{1}{3}$ in reproduction.

heating, so that we cannot suppose that diffusion occurs only upon heating for hardening. We might be justified in so thinking in regard to the high-speed steel, because the hardening temperature is the highest used in all the heatings of the steel, but the temperatures used for rolling this knife steel are 400° F. above the hardening temperature.

Physical proof that there is no pure electrolytic iron remaining in the annealed weld is not lacking. Fig. 19 shows an annealed sample of high-speed steel welded between two pieces of steel containing 0.15 per cent carbon and 5 per cent chromium. This has been fractured by slow, steady pressure, and has broken through the high-speed steel, which

would be stronger than a pure electrolytic iron if it were present in the weld.

Figs. 15 and 16 show respectively the annealed and the hardened and drawn structure of the weld between a die steel (1.6 per cent C; 12 per cent Cr) and a low-carbon iron backing. In Fig. 15 the etch is heavier than usual, and shows the grain boundaries in the weld zone; after hardening and drawing, Fig. 16, there are again signs that the material in the weld zone is not pure iron.

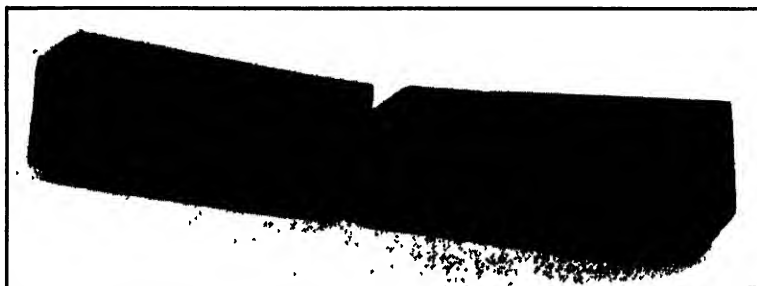


FIG. 19.—HIGH-SPEED STEEL DUO-WELDED BETWEEN 4 AND 6 PER CENT CR STEEL NOT AS STRONG AS DUO WELDS

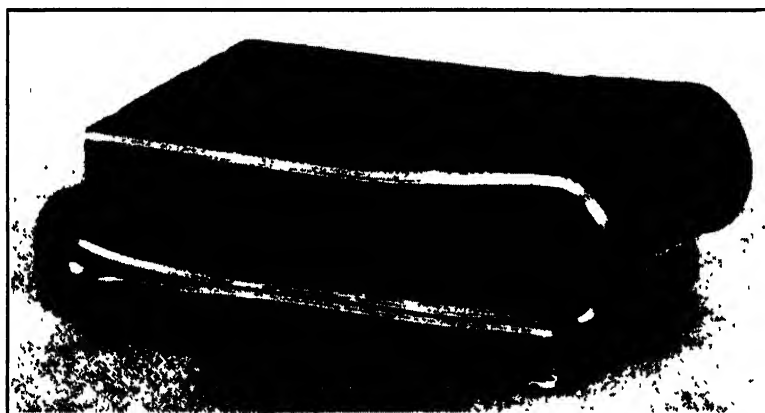


FIG. 20.—COLD BEND TEST ON 18-8 DUO-CLAD.

Fig. 17 shows the weld between 18-8 and a low-carbon iron backing. The sample was cut from a large bar that had been given a commercial water quench from 2000° F. In order to bring out the structure of both the 18-8 and the backing material, the etching was performed in two stages. First, the sample was etched electrolytically for 7 min. in a 10 per cent solution of sodium cyanide, and then for about 6 min. by ordinary immersion in a saturated solution of picric acid. Even this etch does not show the perfection of the weld to advantage, owing to a difference in height that casts a shadow. Fig. 18 shows the same

material at a higher magnification, etched in picric acid only, no attempt being made to bring out the structure of the 18-8. The weld is beautifully diffused, and free from all inclusions.

A piece of iron clad with 18-8 is shown in Fig. 20, bent back twice upon itself under compression while cold, one bend having the 18-8 cladding on the outside, and the other one on the inside. There is no weld rupture. Repeated heatings and quenchings of this 18-8 clad material do not cause the two metals to part.

We have already seen in Fig. 19 that the weld is not the weakest part of one of these composite pieces. But what happens when we force a sample to break through the weld? A severe test is commonly given to composite steel to be used for knife blades, which forces the sample to break through the weld. A transverse section of composite knife stock is cut from the bar, hardened and drawn, and broken by steady pressure applied as shown in Fig. 21a. In order that holes and slots may be freely cut before use, a backing material that will remain soft after the hardening treatment is chosen for this composite knife stock, whereas the carbon-tungsten-chromium steel that is used for the cutting edge has a hardness of 65-C Rockwell. If this sample is bent until it breaks, it will break as in Fig. 21b, because the insert is so hard that it will not bend. When such a break is examined in material that has been welded by the method described in this paper, it is found that grains of the soft backing material adhere to the hard steel, and vice versa. The sample is forced to break at the weld, but hard and soft metals are both torn from their parent metals in making the break.

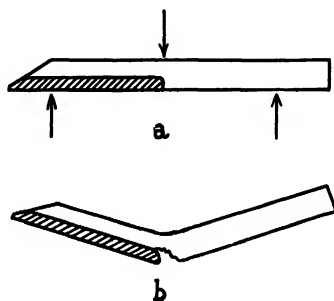


FIG. 21.—BEND TEST USED FOR COMPOSITE KNIFE STEELS.

USES AND LIMITATIONS OUTSIDE THE FERROUS FIELD

This method of welding is applicable to many nonferrous metals, and alloys such as Stellite and Hastelloy, which by its use have been successfully welded to iron backing material. Tungsten carbide and tantalum carbide have so far defied all efforts to pickle them clean enough for iron plating, but further work is planned on this problem.

There is no reason why any metal upon which a truly adherent iron plating can be deposited should not weld to another prepared piece, provided only that such a material would not melt at the welding temperature. Examples of two metals that it would be useless to plate with iron in this process are zinc and lead, as they would be molten at the

temperature at which iron welds to iron, but copper can be successfully iron-plated and then welded. A flash coating of copper to receive the iron plating might be useful on an alloy steel if prevention of carbon migration across the weld is desired.



FIG. 22.—IRON (BOTTOM) DEPOSITED ON COPPER (TOP), DIFFUSED 1 HR. AT 1900° F. $\times 500$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.
Section 45° through bond. Etched in 50 per cent nitric and 50 per cent acetic acids.



FIG. 23.—IRON (TOP) DEPOSITED ON NICKEL (BOTTOM) DIFFUSED 1 HR. AT 1750° F. DIFFUSION ZONE IN CENTER. $\times 1000$, REDUCED $\frac{1}{3}$ IN REPRODUCTION.
Section 45° through bond. Etched in solution of 50 per cent nitric and 50 per cent acetic acids.

Figs. 22 and 23 show respectively the diffusion zones between copper plated with iron and nickel plated with iron, by the method described in this paper, and then heated for 1 hr. at 1900° F. (1040° C.). Fig. 22 shows copper diffused into iron particularly at the grain boundaries.

The alloy thus formed was red in color. Apparently the iron does not appreciably diffuse into the copper; at any rate, not with this time of heat-treatment.

The extent of the diffusion of the nickel into the iron in Fig. 23 may be compared with Fig. 24, which shows the diffusion produced in common commercial practice when sheets of nickel and iron are rolled together and soaked for about 10 hr. in a soaking pit. Notice the narrower diffusion zone in Fig. 24 despite the fact that the material was soaked 10 times longer, and also the globules of oxide.



FIG. 24.—STEEL (BOTTOM) AND NICKEL (TOP) ROLLED TOGETHER. DIFFUSION ZONE IN CENTER.

Held 10 hours in soaking pit after rolling to make the bond. Section 45° through bond. Etched in solution of 50 per cent nitric, 50 per cent acetic acids.

The chemically clean surface upon which the iron is electroplated in this process is the factor that makes for successful diffusion during subsequent heating.

SUMMARY

A new commercial method for producing a true weld between any ferrous metals is described step by step.

The ferrous alloy is first cleaned so as to free it from all oxide film, and while it is in this chemically clean condition it has plated upon its surface a few thousandths of an inch of electrolytic iron. Any subsequent heating to a good red heat will start diffusion between the ferrous alloy and the electrolytic iron. This iron-plated ferrous alloy may be welded to a piece of soft iron, or to any other ferrous alloy similarly iron-plated, by placing the two prepared faces in contact, heating to a good red heat, and applying pressure. If, during this heating, precautions are taken to

guard against scaling of the two prepared surfaces, a weld will be produced that is oxide free. The weld has taken place between two clean iron surfaces, each held by diffusion to its ferrous-alloy backing.

This weld is strengthened by each subsequent heating, until elements from the ferrous alloys have diffused entirely through the electrolytic-iron weld zone. Properly prepared and assembled composite billets welded by this method are free from nonmetallic material in the weld zone, and the welded materials fuse one into the other as a graduated alloy.

ACKNOWLEDGMENTS

The author particularly wishes to thank Mr. P. A. E. Armstrong for his many suggestions and his helpful criticism during the writing of this paper, and for his help in the preparation of the bibliography. Thanks are also due to Mr. W. G. Kuntz, who prepared and examined the microstructures and who took most of the photomicrographs

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DISCUSSION

(Erle G. Hill presiding)

P. A. E. ARMSTRONG,* Westport, Conn. (written discussion).—This is the first paper I have seen on the subject of clad metals that has shown how the work is actually done. Very little has been published on the subject, and what has been

* Consulting Engineer.

published is largely on the order of a vague description of the process, what the metal looks like when it is welded, and some applications.

Mr. Grimshaw has brought out admirably the diffusion welding that takes place between the facing metal and the backing metal. In my experimental and commercial work in the production of the process and its development, I have found it practically impossible to determine just what the diffusion is in the way of analysis because the diffusion line is thin and it is impossible to machine away the backing and the facing to leave only the diffusion zone; therefore chemical analysis has been impossible. One way in which diffusion can be positively located is by microscopic observation as Mr. Grimshaw has shown in his paper.

Iron is the only metal that lends itself to successful welding. If nickel plating is employed, there is formed on the surface of the nickel a very thin layer or film, which prevents welding—presumably an oxide layer. If copper is employed, welding can be satisfactorily done at a low temperature because of the low melting point of the copper, but copper has the disadvantage of tending to embrittle the weld zone by too much copper diffusion. If the copperplate is heated to temperatures of 2100° to 2200°F., naturally the copper layer becomes molten and partly squeezes out the remainder, diffusing to such an extent that the copper solution in iron is precipitated, thereby weakening the weld zone. A plate of nickel superimposed upon a plate of mild steel can be welded by heat and pressure, but there is always in such a weld a goodly quantity of oxide, whereas if the nickel plate is plated with electrolytic iron and then such nickel plate superimposed upon a ferrous backing plate, preferably electroplated with iron, an excellent weld is produced and the electrolytic iron diffuses with the nickel and no oxide is present. Under these circumstances I feel that I am correct in stating that iron seems to be by far the best metal to use for making the diffusion weld bond.

If molten low-carbon steel is cast against the surface of an alloy steel or nickel insert, little or no welding takes place and the surface oxide on the molten metal becomes entrapped, as it has a tendency to stick to the alloy steel or nickel insert, and not roll up towards the top of the ingot; whereas, if the inserts are electroplated with iron, the molten mild steel lies against the electrolytic iron and rises against it very nicely, and very little oxide seems to be entrapped. Such an ingot, when rolled down, is very free from oxide. The electrolytic iron adheres to the cast metal in an excellent manner and, of course, the electrolytic iron diffuses to the alloy or nickel insert without difficulty. The weakness, if any, is therefore between the electrolytic iron and the backing, and not between the insert and the electrolytic iron.

For practical purposes the casting method is as good as the assembly method, but if the very finest welds are to be made, the assembly method is preferable. When making very large plates, thicknesses of 2 or 3 in. or more, the casting method is more suitable because of the difficulties of holding the assembly together and the losses that must take place in the trimming of the portion that has been used for holding the assembly together during rolling.

Recently the largest clad plate that has ever been made was successfully rolled. It weighs some 4500 lb. and was spun into an elliptical head, which is a very hard job on a solid material because of the gathering that must take place, as the head is so deeply dished. With the clad material made by the process that Mr. Grimshaw has explained, the head was dished or spun without difficulty. There was a gathering of over $\frac{1}{4}$ in. in thickness, yet there was no sign in any place of the weld letting go, and test pieces taken off the dished head at the edges showed the weld to be perfect and in no way hurt or strained by the spinning operation. There seems to be no limit to sizes and thicknesses of clad metal that can be made by this process except that enforced by the mill dimensions.

As an instance of the high diffusion of alloy steels, high-cobalt high-speed steel diffuses very rapidly and if about 0.006 in. of electrolytic iron is used, the cobalt high-speed steel will diffuse during the process of heating or rolling through about 0.006 in. electrolytic iron, and welding will not take place. However, about 0.015 in. of electrolytic iron is sufficient, and no trouble is experienced at all in the welding. Some other classes of alloy steels do not diffuse so rapidly and 0.005 to 0.010 in. is sufficient. Generally speaking, about 0.006 to 0.020 in. is sufficient to take care of all of the alloy steels except perhaps the high-cobalt high-speed steels.

I have had no difficulty with this process in producing large plates having a cladding of 30 per cent chromium low-carbon steel cladding, and of course no trouble with the 16 to 20 per cent chromium low-carbon steel cladding. The high-chromium high-nickels can be readily clad by the process and just as readily as the usual 18-8.

Since this process has been in commercial use I have not learned of any failure in the weld. I have had difficulties, of course, in determining the correct method of making assemblies, but the failures from such difficulties have been very small. I feel I am safe in stating that I do not think there is an alloy steel that is capable of being rolled that cannot be welded successfully to any ferrous backing material that of itself is capable of being rolled. Under these circumstances this new process opens up fields for clad materials that heretofore have been considered impossible.

The larger the plate, the less the amount of autogenous welding, which adds to the strength of the tank and cuts down the cost. Most of the cladding that has been used for tanks, and particularly dished heads, has looked something like a cut pie, because of the number of segments that had to be employed, whereas this process will enable large plates to be used, segment cutting now becomes unnecessary and at the most a very large head can now be made in two pieces. Up to now the large heads have been made in one piece, but larger work is contemplated which exceeds the size of the rolling mill rather than our welding abilities.

The weld zone is very strong, and in making physical tests on these welds a 1-in. wide test bar is cut through the cladding down to the backing, and then a 1-in. square is left and the backing is cut down to the cladding, and the whole then pulled in a tensile testing machine. In every instance the clad material has broken in the cut portion, showing absolutely no separation of the cladding in the 1-in. square section. It is difficult to interpret this in pounds per square inch because the total amount of pull that can be given to a test sample must be governed by the thickness of the cladding. Obviously a greater load can be given to a cladding $\frac{1}{4}$ or $\frac{1}{2}$ in. than can be given to a similar cladding $\frac{1}{8}$ in. thick. This form of testing is very useful because not only is there a pull upon the surface of the cladding, but there is a shearing action as the test piece offsets at an angle during pulling. If the weld is not good, there would be a tendency for this askew-wise pulling to lift up the cladding in the weld zone. However, the weld is so excellent that such a failure has not yet happened and I can see no reason for it ever doing so.

E. E. THUM,* Cleveland, Ohio.—I want to compliment Mr. Armstrong and Mr. Grimshaw for developing this process. There are, of course, several other methods of making ply metal, which have been commercialized recently, and I myself am more interested in the stainless-clad material than in other combinations. Among the other well-known methods is one where a thin sheet of ingot iron is sandwiched between the soft steel backing and the stainless steel, and these are heated to welding temperature and rolled or forged to a unit. Another is a plain "casting-in" process.

* Editor, *Metal Progress*.

Proponents of these and probably of other processes are quite sure they always get a perfect weld. However, some of the samples I have seen look very far from being perfect. In fact, had I had anything to do with selecting samples of that sort, I would have kept the ones I saw under lock and key rather than show them to prospective customers. Alongside of these samples were also pieces of fabricated ware which had been badly beaten up under a hammer and apparently the weld, although obviously it was not a 100 per cent joint, was sufficiently good to stand the deformation that had been given to it in that brutal treatment.

I would be interested to learn of actual service experience with stainless-clad material, especially at moderate temperatures. The reason for promoting clad metal, of course, is that the ultimate cost of a piece of heavy equipment is less than it would be if built of a solid stainless metal. Such equipment of clad stainless steel (and I am speaking of 18-8 now) would probably have to operate at moderately high temperatures. The coefficients of expansion of 18-8 and plain carbon steel are so greatly different (18-8 being 40 to 45 per cent greater) that the user will get into serious troubles unless that particular feature is well taken care of. This is a common experience in the oil industry with 18-8 condenser tubes in mildly corroding solutions when these alloy tubes are installed in a condenser shell that has been designed for the use of plain carbon steel tubes. This indicates that a rather slight amount of temperature stress set up by a few hundred degrees Fahrenheit is enough to cause corrosion cracking in the 18-8 under very mild conditions in a very short time. Would not the same thing occur in bimetal sheet heated to, say, 300° F.? I would be interested to discover service records of such equipment where the corrosion conditions are relatively severe. The prospective user will be reassured to know that no undue stress corrosion has ensued in those cases.

G. E. DOAN,* Bethlehem, Pa.—The use of the word "new" seems perhaps to imply fundamentally new. Although this process appears to be quite sound and useful, I think it is perhaps misleading in implication to call it new. It is new in the combination of steps, but when it is resolved we find it is not a new method of actually producing a weld. Certainly the plating and heating to cause diffusion are not new, and certainly the pressure welding of coated objects is not a new method of welding. That, however, is obvious.

The question I want to ask is this: When the coated objects are placed in contact and arc-welded, it would seem to me that this intense heating along the edges would produce an oxide film just inside those edges, oxidation of the pure iron surfaces. I wondered if that had been found.

P. A. E. ARMSTRONG.—Three-eighths of an inch.

G. E. DOAN.—Does that not interfere with the pressure welding at the edges?

P. A. E. ARMSTRONG.—No, because the two surfaces to be joined together by the same weld are held very tightly together by a very powerful vise operated by jacks. With plates a slight oxide along the edges makes no difference as this is trimmed off later, and with bars the small amount of discoloration at the edges, caused by the heat, is not sufficient to prevent welding between the two electrolytic iron surfaces. The oxide that forms is merely a color oxide, and in many instances, and particularly with carefully prepared surfaces, there is no discoloration between the two contacting surface edges.

L. C. GRIMSHAW (written discussion).—I should first like to comment upon the process Mr. Thum mentions, in which a weld is made by sandwiching a thin sheet of ingot iron between a mild steel backing and a stainless steel. The thin sheet of

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ingot iron introduces a relatively wide zone of weakness into the weld. There is oxide on the surface of the stainless steel before the weld is made, and only great elongation will break up this oxide film and allow elements to begin to diffuse across and strengthen the weld zone. I believe it is a fact that satisfactory clad sheets are made by that method only when the elongation is very great, and that such a thing as a clad sheet 2 in. or more thick has not yet been made.

By the process described in my paper, good welds can be made with very little reduction, and therefore thick plates are possible. Plates $2\frac{1}{8}$ in. thick, and down to thin gages, have already been made. Moreover, no matter how little reduction the steel is given to make the weld, the weld zone is only a few thousandths of an inch thick. Because diffusion can start from the steel into the electrodeposited iron while the assembly is being heated for rolling, then as soon as rolling has made the weld, complete diffusion across the weld zone may be completed by heating for a short time thereafter. Slow cooling or annealing completes it. The zone of weakness (pure iron) is eliminated.

One of the best tests that the weld of a clad sheet receives is the ordinary commercial heat-treatment and subsequent cold straightening. A stainless-clad sheet curls up into a cylinder when cooling, and if it then withstands cold straightening, the weld is good. All the clad sheets made by the method described in this paper, including 18-8 with titanium and 28 per cent chrome-iron cladding, have withstood this. Many have been dished into full elliptical heads by spinning, without a single failure. It is well known that it is more difficult to spin a head than it is to press it, and for very large, full elliptical heads the open-hearth steel is taxed to its maximum extent by spinning. Our clad plates have withstood this tremendous amount of hot-working without any detrimental effect on the weld. When the heads are spun there is a gathering of metal, which materially increases the thickness at the rim of the elliptical head, and this upsetting action will rupture any weld that is not perfect.

I appreciate the point Mr. Thum brought up about the need for service records of 18-8 clad sheet used under conditions that may cause stress corrosion of the 18-8. If the thermal expansion difference between the 18-8 and its backing at temperatures of only a few hundred degrees Fahrenheit does cause stresses resulting in the corrosion of the 18-8, I believe we should use some other steel for cladding. An 18-8 steel with additions of 5 per cent manganese and 2.5 per cent copper remains fully austenitic after being subjected to great strain, and has the added advantage of not having to be heated over 1600°F. to make it fully austenitic, and stable enough to withstand any cold straightening, fabricating or autogenous welding. It should also suffer no damage from expansion stresses in service.

The reason I called this process new is because I consider it is the only process that aims at the elimination, in every weld, of any zone of weakness. This is accomplished by thorough diffusion, and by avoidance of oxides. Although in another process Armco iron has been put in between the surfaces to be welded, I do not consider that real diffusion can always take place. At least, from my experience, after the weld has been made by rolling it takes hours in a soaking pit to get diffusion across such a bond. Mr. Doan's question as to heat oxidation has been answered by Mr. Armstrong. In this method we try to eliminate *all* oxide in the weld, therefore we use every commercially practical precaution to guard against its introduction, but if we do get a little heat-tint oxide here and there along the edges, mostly due to imperfect fit between the pieces, we still get a weld between the iron-plated surfaces. It is never a thick oxide, such as scale, and does not prevent diffusion starting from the cladding (and from the backing if it has been ironplated also) into the electrolytic iron during heating for rolling. After rolling this oxide is broken up, and diffusion can be completed right across, during slow cooling or heat-treating, because the weld has now been made.

Action of Solutions of Sodium Silicate and Sodium Hydroxide at 250° C. on Steel under Stress

By W. C. SCHROEDER* AND A. A. BERK†

(New York Meeting, February, 1936)

PRACTICAL experience has shown that at elevated temperatures solutions containing sodium hydroxide may attack stressed steel in a manner that cannot be explained in terms of ordinary corrosion. Because the ductility of the metal has been greatly reduced during the reaction, the entire phenomenon is usually called "embrittlement." Thus, after several years of operation caustic evaporators have been so badly embrittled that rivets could be cracked off with the blow of a hammer. Since fine intergranular cracks are almost always present in the zone of fracture, it has often been assumed that a process of selective corrosion in grain boundaries was responsible for the failure, although this has not been clearly proved experimentally. Concentrations of sodium hydroxide below those necessary for the uniform, rapid attack of the steel surface are reported to be most effective in producing embrittlement^{2,3}.

In the operation of steam boilers a similar type of failure has been found, mainly in riveted seams or other capillary spaces where the solution may concentrate and where high stresses may also exist. It is believed that in such localized areas the dissolved solids may reach a value many times the few hundred parts per million prevalent in the body of the boiler. While this type of boiler failure has been the subject of investigation for a period of 20 years¹, an understanding of its mechanism and a rational basis for complete protection have not yet been secured. To procure this information the present investigation was

Manuscript received at the office of the Institute Dec. 2, 1935. The essential data in this paper, indicating the effect of the sodium silicate-sodium hydroxide solutions on steel, were originally reported on Oct. 1, 1935, to a subcommittee of the Joint Research Committee on Boiler Feedwater Studies. The discovery of the effect of these solutions resulted from the extensive investigation made of the embrittlement of steel at the U. S. Bureau of Mines during the past two years.

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times weight added on lever) was found to be within 2 per cent of the value indicated by the testing machine throughout the entire load range.

The test piece consisted of a tubular specimen closed at one end and the load was applied by means of a rod passing through the center. This specimen eliminated the necessity for a packing gland, thus obviating both leakage and the possibility that the gland might exert sufficient friction to cause a serious error in the load actually applied to the test piece. The fact that the tubular specimen, as compared to a solid one, had a higher ratio of surface exposed to solution to cross-sectional area of metal was also considered to be an advantage.

The two types of test specimen used are shown in Fig. 2. The one indicated as concentric-ground was carefully prepared to insure a uniformly distributed tensile load, with a minimum of bending. The reduced section was ground with a fine emery wheel running parallel to the length to eliminate surface scratches perpendicular to the direction of application of the load. In the grooved specimens the outer and inner cylindrical surfaces were concentric, but the groove was cut on an axis displaced 0.010 in. from the axis of these surfaces. The radius at the base of the groove was 0.0056 in. and the maximum depth of the groove was

TABLE 1.—Average Physical Properties of the Boiler-flange Steel at Room Temperature and 250° C.*

Temperature, Deg. C.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent	Reduction of Area, Per Cent
Room	28,000	58,000	40	63
250.....	21,000	69,000	33	53

* Tests carried out on Standard A.S.T.M. specimens. A.S.T.M. Standards (1933) Pt. I, 935.

TABLE 2.—Chemical Analysis of Boiler-flange Steel*

CONSTITUENT	PER CENT
Carbon.....	0.17
Manganese	0.47
Phosphorus.....	0.021
Sulfur.....	0.039

* Ladle analysis supplied by manufacturer.

0.025 in. The test pieces were machined from a 1-in. plate of boiler-flange steel prepared by the Carnegie Steel Co. The physical properties of the steel in the region from which the test specimens were taken are shown in Table 1 and the chemical analysis in Table 2.

All of the tests described in this paper were conducted at 250° C., corresponding to a gage pressure for water of 38 atmospheres (482° F., 561 lb. per sq. in.).

TESTS WITH CONCENTRICALLY GROUND SPECIMENS

Two series of tests were carried out with concentrically ground specimens; the first to compare the action of pure sodium hydroxide solutions with the action of water, and the second to determine the specific effect of added sodium silicate.

Effect of Water and Sodium Hydroxide Solutions on Concentrically Ground Specimens

The results in Table 3 indicate that the ground specimens required a tensile load of about 82,500 lb. per sq. in. to produce failure in short-time

TABLE 3.—*Short-time Tests in Embrittlement Bombs to Determine Breaking Load for Concentrically Ground Specimens*

TEMPERATURE, 250° C.		BREAKING LOAD, LB. PER SQ. IN.
NaOH CONCENTRATION, GRAMS PER 100 GRAMS H ₂ O		
Water.....		82,700
		82,100
25.....		83,300
		82,100
Average.....		82,550

tests under the progressively increasing load. These tests were conducted by placing the test piece and solution in the bombs, bringing the temperature to 250° C., then slowly adding weights to the end of the lever arm until failure occurred. The steel was under load about 2 hr. The fact that the tensile strength indicated in this table is higher than that shown for the standard solid specimens at 250° C. in Table 1 may be attributed to the differences in shape of specimen and rate of loading. These results were checked in an oil bath in the tensile-strength testing machine, and good agreement was obtained. It should be noted in Table 3 that contact with a concentration of sodium hydroxide of 25 grams per 100 grams of water did not lower the short-time breaking strength as compared to the value obtained in water.

TABLE 4.—*Resistance to Failure of Concentrically Ground Specimens in Water and Sodium Hydroxide*

TEMPERATURE, 250° C.

NaOH Concentration, Grams per 100 Grams H ₂ O	Average Applied Stress, Lb. per Sq. In.	Duration of Test Days
Water.....	75,000	43
25.....	75,000	21
25	75,000	43

The results in Table 4 show that three specimens in water and sodium hydroxide solutions, subjected to a steady load of 75,000 lb. per sq. in., did not fail in periods up to 43 days. Comparison of Tables 3 and 4 indicates that this average applied stress is within 7500 lb. per sq. in. of the load required for failure. From these results it can only be concluded that contact with a solution of sodium hydroxide, under the conditions and concentrations indicated, does not produce any marked effect on the tensile load the steel can sustain.

These results are at complete variance with those obtained by Straub², who found that tensile loads slightly above the room-temperature yield point would cause failure when the steel was in contact with approximately this concentration of sodium hydroxide at 500-lb. gage pressure. Ulrich³, in Germany, found, however, that steel under these conditions would carry for a long period a tensile load more than 50 per cent higher than the room-temperature yield point. Two investigations conducted in the United States from 1932 to 1934* also indicated that sodium hydroxide in concentrations up to 50 grams per 100 grams of water did not produce a measurable effect on the ability of steel specimens to carry a tensile load.

*Effect of Solutions of Sodium Silicate and Sodium Hydroxide on the
Concentrically Ground Specimens*

In the first attempt to explain these differences samples of steel were exchanged with Professor Straub, but the respective results were unaffected. Professor Straub later advised the authors that in two tests with chemically pure sodium hydroxide he had been unable to produce failure of his specimens under conditions that previously had resulted

TABLE 5.—*Failure of Concentrically Ground Specimens in Commercial Sodium Hydroxide*

25 GRAMS NAOH PER 100 GRAMS WATER. TEMPERATURE, 250° C.

Average Applied Stress, Lb. per Sq. In.	Failure, Hr.	No Failure, Days
70,000	12	10
70,000	55	
70,000	17	
65,000	32	
65,000	29	
60,000*	58	
55,000*	56	
50,000		

* Failure at shoulder.

* Private communication.

in rapid failure when he used commercial sodium hydroxide.⁴ The latter grade of material had been used by him in most of the tests reported².

Professor Straub kindly provided the authors with some of this material. The results of a series of tests with it on concentric-ground specimens are shown in Table 5. Failure occurred in a few hours at loads as low as 55,000 lb. per sq. in., whereas no failure had previously been obtained with chemically pure sodium hydroxide in 43 days under a load of 75,000 lb. per sq. in. Some of the specimens (Table 5) failed at the radius near the top or bottom instead of the ground section in the middle. This probably resulted from a slight concentration of stress at these radii, but since microscopic examination of such specimens indicated that the ground section was also cracked in almost every case this is not believed to be important. From the results shown in Table 5 it may be concluded that either the commercial sodium hydroxide contained some impurity, which caused or perhaps catalyzed the reaction to produce failure, or the chemically pure solution contained some substance that inhibited the reaction. The weight of evidence was toward the first view, and subsequent results proved that this was correct.

TABLE 6.—*Analysis of Commercial Sodium Hydroxide*

QUANTITATIVE ANALYSIS		QUALITATIVE ANALYSIS	
Component	Per Cent	Component	Per Cent
NaOH	95.9 ^a	Heavy metals (Pb-Hg, etc.)	None
Na ₂ CO ₃	2.10 ^b	Arsenic.....	None
NaCl	0.57	Sulfides	None
Na ₂ SiO ₃	0.64	Magnesium	None
R ₂ O ₃ (Al ₂ O ₃)	0.05	Peroxide.....	Tr
(Fe ₂ O ₃).....		Cyanides	None
Ca	Tr	Sulfates.....	Tr

^a Not corrected for R₂O₃ or Na₂SiO₃.

^b Determined by evolution.

An analysis of the commercial sodium hydroxide is given in Table 6. A quantitative determination was performed for all components present in appreciable concentration, and a qualitative analysis was made for a number of other components. Quantitative analysis of the chemically pure sodium hydroxide, which was stored as a saturated solution in a paraffined bottle, indicated 0.2 per cent sodium carbonate and 0.02 per cent sodium silicate. These values are approximately $\frac{1}{10}$ and $\frac{1}{30}$ of the amounts of the same compounds found in the commercial sodium hydroxide. The chemically pure material contained negligible quantities of sodium chloride and R₂O₃.

With these analyses as a guide, the salts present in the commercial sodium hydroxide were added to solutions of the chemically pure substance, with the results recorded in Table 7, showing that only the solutions that contained sodium silicate caused failure. In the last sample, when sodium silicate alone was added to the sodium hydroxide solution, failure also resulted.

TABLE 7.—*Failure of Concentrically Ground Specimens in Solutions Containing Sodium Silicate and Sodium Hydroxide*

TEMPERATURE, 250° C. AVERAGE APPLIED STRESS, 70,000 LB. PER SQ. IN. NaOH CONCENTRATION, 25 GRAMS PER 100 GRAMS H₂O

Added Salts	Grams per 100 Grams H ₂ O	Failure, Hr.	No Failure, Days
Na ₂ CO ₃	0 5		4
NaCl.....	0 13		
Na ₂ CO ₃	0 5		6
NaCl	0.13		
Na ₂ CO ₃	0 5		7
NaCl.....	0.13		
Al ₂ O ₃ ^a	0 05		
Na ₂ CO ₃	0 5	34*	
NaCl	0 13		
Al ₂ O ₃ ^a	0 05		
Na ₂ SiO ₃ ^b	0 2		
Na ₂ CO ₃	0 5	21	
NaCl.....	0 13		
Na ₂ SiO ₃ ^b	0.2		
Na ₂ SiO ₃ ^b	1 5	77	

* Added as aluminum chloride.

^b Baker's water glass 40 per cent solution, used to introduce silica into bombs.

* Failure at shoulder.

The data in Table 8 indicate the effect of varying the silica concentrations on the failure of the specimens. With concentrations much below 0.15 gram per 100 grams of water and 25 grams of NaOH per 100 grams of water, failure did not occur in periods up to 10 days. As the silica concentration was increased, the time for failure tended to become somewhat shorter, but at 10 grams per 100 grams of water this effect was apparently reversed. Too much reliance cannot be placed on small differences in the time required for failure, however, as this value is doubtless affected by a number of rather uncontrollable factors. Table 8 also shows that failure can be secured at loads as low as 55,000 lb. per sq. in.

The fact that the one sample that failed at this load also contained sodium carbonate and sodium chloride does not necessarily indicate that these salts exert an appreciable effect on the results, since this stress is apparently near the border line for failure or no failure.

TABLE 8.—*Effect of Stress and Sodium Silicate Concentration on the Failure of Concentrically Ground Specimens*

25 GRAMS NaOH PER 100 GRAMS H₂O. TEMPERATURE, 250° C.

Average Applied Stress, Lb. per Sq. In.	Na ₂ SiO ₃ , Grams per 100 Grams H ₂ O	Failure, Hr.	No Failure, Days
70,000	0 077		10
70,000 ^a	0.15	32	
70,000	0 40	44	
70,000	1.7	10	
70,000	5 0	8	
70,000	10 0	135	
70,000	10.0	80	
60,000 ^a	3.0	135	
60,000	3 0	120	
55,000	0 16		10
55,000 ^a	0 16 ^b	152	

^a Failure at shoulder.

^b Solution also contained 0.52 grams Na₂CO₃ and 0.11 grams NaCl per 100 grams H₂O. Baker's c.p. sodium silicate (Na₂SiO₃·9H₂O) used to introduce silica into bombs.

It will be noticed from Tables 7 and 8 that the sodium silicate could be introduced into the bombs either from a solution of water glass or from chemically pure Na₂SiO₃·9H₂O dissolved in water without producing any apparent differences in the results.

A large number of microscopic examinations have been made of specimens broken in sodium hydroxide solutions and in sodium silicate-sodium hydroxide solutions. One of the chief characteristics of the action of the silicate-hydroxide solutions is the production of a large number of almost completely intercrystalline cracks in the steel.

From these results it seems entirely safe to conclude that sodium silicate-sodium hydroxide solutions produce an effect on steel in tension entirely different from or greatly accelerated beyond that produced by sodium hydroxide alone.

TESTS WITH ECCENTRICALLY GROOVED SPECIMENS

In practice, embrittlement is found to occur most frequently in regions where the steel can suffer a local stress concentration; for example, under the head of a rivet or around a rivet hole, where it is likely that the

stress will not be pure tension but tension combined with bending. Similarly, in the tests recorded in Tables 5, 7 and 8, a total of six specimens failed, not in the region of high, uniformly distributed stress but in the region of nonuniform stress of unknown magnitude, at the shoulders of the test pieces. The eccentric-grooved specimen was intended to produce similar conditions of stress concentration with a test piece that was as reproducible as possible. The results indicate that both chemically pure sodium hydroxide solutions and sodium silicate-sodium hydroxide solutions have a much more pronounced effect on this specimen with localized stress than on the concentric-ground specimen with more uniform stress distribution.

TABLE 9.—*Short-time Tests in Embrittlement Bombs to Determine Breaking Load for Eccentrically Grooved Specimens and Load They Will Carry in Water Alone*

ALL SPECIMENS IN WATER. TEMPERATURE, 250° C.	
AVERAGE APPLIED STRESS, LB. PER SQ. IN. ^a	NO FAILURE, DAYS
73,500	Breaking test
70,200	Breaking test
70,000	Breaking test
65,000	15
65,000	15

^a Calculated for area of metal at base of groove.

TABLE 10.—*Failure of Eccentrically Grooved Specimens in Solutions of Chemically Pure Sodium Hydroxide^a*

25 GRAMS NaOH PER 100 GRAMS H₂O. TEMPERATURE, 250° C.

Average Applied Stress, Lb. per Sq. In. ^b	Failure, Hr.	No Failure, Days
67,400	13	
68,600	4	
65,000	8	
65,000	6	
62,000	18	
62,000	80 ^c	
59,000	6	
59,000	19	
55,000	37	
55,000	36	
50,000	21	
50,000		12
45,000		10

^a Na₂SiO₃ present is 0.02 per cent of NaOH concentration.

^b Calculated for area of metal at base of groove.

^c Specimen stopped and reloaded after 50 hours.

TABLE 11.—*Failure of Eccentrically Grooved Specimens in Solutions of Sodium Silicate and Sodium Hydroxide*25 GRAMS NaOH PER 100 GRAMS H₂O. TEMPERATURE, 250° C.

Average Applied Stress, Lb. per Sq. In. ^a	Na ₂ SiO ₃ , Grams per 100 Grams H ₂ O	Failure, Hr.	No Failure, Days
40,000	1.6	73	10*
40,000	0.40	40	
40,000	0.16	21	
35,000	0.16	33	
30,000	0.16 ^b	60	
30,000	0.16	93	
25,000	0.16 ^b	72	
25,000	0.16		
25,000	0.40	190	
20,000	0.16 ^b	75	
20,000	0.32	78	

^a Calculated for area of metal at base of groove.^b Commercial sodium hydroxide referred to in Table 6.^c Microscopic examination showed embrittlement cracks.TABLE 12.—*Failure of Eccentrically Grooved Specimens in Solutions Derived from Pure Quartz and Sodium Hydroxide*25 GRAMS NaOH PER 100 GRAMS H₂O. TEMPERATURE, 250° C.

Average Applied Stress, Lb. per Sq. In	Na ₂ SiO ₃ , Grams per 100 Grams H ₂ O	Failure, Hr.
40,000	0.46	43 ^a
30,000	0.30	21 ^b

^a 99.4 per cent pure SiO₂. Furnished by Eimer and Amend.^b Brazilian quartz. Furnished by Foote Mineral Co. of Philadelphia.

The first three values in Table 9 give the load required in short-time tests to break the specimen in water in the bombs. The load was progressively increased in these tests during periods ranging from about 15 to 30 min. The last two results in the table show that the eccentric-grooved specimen will sustain a tensile load of 65,000 lb. per sq. in. in water for at least 15 days. Table 10 shows that the stock solution of chemically pure sodium hydroxide that contained only 0.02 per cent Na₂SiO₃ markedly reduced the load that could be sustained, failure occurring at loads as low as 50,000 lb. per sq. in. There was some tendency for the time of failure to increase as the load decreased, but this was not regular or marked.

From these results it is not apparent whether the sodium hydroxide alone was responsible for the lower load that could be carried or whether

this effect arose from the 0.02 per cent Na_2SiO_3 present. It is hoped to determine this before the investigation is concluded.

Table 11 shows the effect of additions of sodium silicate to these sodium hydroxide solutions. Failure was produced at loads as low as 20,000 lb. per sq. in. This is a striking example of the effect of these silicate-hydroxide solutions; this specimen, which has a breaking load of approximately 70,000 lb. per sq. in. in water, will not even sustain a load of 20,000 lb. when in contact with the solution containing both sodium hydroxide and sodium silicate. Three tests are included in this table to indicate the effect of the commercial sodium hydroxide which contained 0.64 per cent sodium silicate.

Tables 7 and 8 showed that water glass and c.p. sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) had about the same effect in producing failure. The two results in Table 12 were collected to eliminate the possibility of the introduction of any impurity with the sodium silicate. Samples of pure quartz were secured from two different sources, fused with the c.p. sodium hydroxide in nickel crucibles, and dissolved in water, and this solution was then used to introduce the silica in the bombs. Failure occurred in approximately the same time as with the silicate solutions previously employed, so that it seems safe to conclude that the latter contained no impurities that produced any marked effect in the reactions.

TABLE 13.—*Effect of Sodium Hydroxide Concentration on Failure of Eccentric-grooved Specimens*

Average Applied Stress, Lb. per Sq. In.	Concentration, Grams per 100 100 Grams H_2O		Failure, Hr.	No Failure, Days
	NaOH	Na_2SiO_3		
65,000	10			12
65,000	10			12
60,000	10	0.75	54	
60,000	10	0.30	50	
60,000	7.5	0.75		14
60,000	7.5	0.30	166	
60,000	7.5	0.15	120	
60,000	5.0	1.9 ^a		10
60,000	5.0	0.75 ^a		10
60,000	5.0	0.30		10

* When removed from the bomb, specimens were found to be covered with a very tightly adhering scale.

Table 13 shows the effect of solutions containing less than 25 grams of sodium hydroxide per 100 grams of water on the failure of the specimens. The first two tests with the c.p. sodium hydroxide, which contained only 0.002 gram of sodium silicate per 100 grams of water, show that the

specimen would not fail at a load of 65,000 lb. per sq. in. With the same concentration of sodium hydroxide and the additions of sodium silicate, failure occurred in a few hours at 60,000 lb. per sq. in. With 7.5 grams of sodium hydroxide and sodium silicate, failure occurred in two tests, but with 5 grams of sodium hydroxide failure was not encountered in three tests. These results, which are rather preliminary, would indicate that 7.5 grams of sodium hydroxide is about the lowest concentration that will produce a measurable effect on the eccentric-grooved specimen at these concentrations of sodium silicate.

At the lowest concentration of sodium hydroxide the formation of a smooth, adherent scale, which appeared to be an iron silicate, may account for the fact that there was no failure. This silicate scale may have been sufficient to protect the steel from reaction with the solution.

CONCLUSIONS

1. At 250° C. sodium hydroxide concentrations up to 25 or 50 grams per 100 grams of water do not produce any significant effect on the tensile load that steel specimens will sustain.

2. Additions of small amounts of sodium silicate to the sodium hydroxide greatly reduce the tensile load that can be carried.

3. On specimens subject to both tension and bending with a line of stress concentration the load that could be carried at 250° C. was reduced from 65,000 lb. per sq. in. in water to less than 20,000 lb. per sq. in. in sodium hydroxide-sodium silicate solutions.

4. Microscopic examination of the specimens that failed in the sodium hydroxide-sodium silicate solution has indicated that one of the characteristic effects of the presence of the silicate was the production of a large number of fine, intercrystalline cracks in the metal near the fracture.

The failure to recognize the part played by sodium silicate in the embrittlement of steel and the use of sodium hydroxide solutions that contained from very little to relatively large amounts of sodium silicate has resulted in many conflicting data regarding this type of failure. With a knowledge of the action of the silica, it is now possible to correlate many of these data. Up to the present no explanation backed by adequate experimental evidence has been advanced as to the reactions that produce embrittlement. Considerable evidence is available to show that the hydrogen released by the action of the solutions on the steel is a very important factor. It is difficult, however, to see the exact part played by silica in such a process. It is hoped to be able to determine the mechanism of the reactions during further investigations.

ACKNOWLEDGMENTS

The authors wish to thank the many companies and individuals that have contributed to the support of this investigation and to acknowledge

the constant guidance of Mr. J. H. Walker, chairman of the subcommittee of the Joint Research Committee for Boiler Feedwater Studies sponsoring this investigation, and of Mr. Everett P. Partridge, formerly supervising engineer of the Nonmetallic Minerals Experiment Station of the Bureau of Mines, who have contributed greatly to the progress of this research.

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DISCUSSION

(Erle G. Hill presiding)

E. G. HILL,* Coatesville, Pa.—I am sure that steelmakers and fabricators of boilers and pressure vessels find this an interesting subject. Many attempts are now being made to learn something about the phenomenon of caustic embrittlement and hydrogen blistering. Those who have seen a piece of steel in which hydrogen has penetrated as far as $\frac{1}{8}$ in. and then built up a pressure great enough to rupture the steel have an idea of the tremendous force acting.

H. F. MOORE,† Urbana, Ill. (written discussion).—Messrs. Schroeder and Berk report very low values of *average* stress in specimen to cause cracking in specimens with an eccentric groove turned round them. I cannot see that these low average stresses are of any great significance. The groove itself would be a decided "stress raise," and the fact of its eccentricity would make the stress-raising effect still worse (probably it would be better to say the stress-raising effect *might* be still worse). The *maximum* stress in the specimen would be significant rather than the average, and that maximum stress is not known, because of the two factors of eccentricity and the sharp groove. Effect of eccentricity might be computed approximately on the assumption of perfect gripping, which is very unlikely, but it would be very difficult to compute effect of groove; in fact, quite impossible, unless all dimensions of groove were given.

J. F. CHITTUM‡ AND H. W. RITCHEY,‡ Lafayette, Ind. (written discussion).—We have been investigating the nature of the caustic attack of iron for several years, and check the results obtained by Schroeder and Berk, with possibly one exception, wherever the experiments have overlapped. Also we feel that we are in a position to announce results that supplement those of the authors and that should be mentioned in a discussion of their paper.

The possible exception should be cleared up first. The experiments reported at the bottom of page 391 seem to give the impression that there is no attack of iron by *pure* caustic that is different from that of pure water. In some of our experiments we have worked with Armco iron and Mallinckrodt analytical reagent sodium hydrox-

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‡ Department of Chemistry, Purdue University.

ide in a stainless steel autoclave. At steam pressures as low as 200 lb. per sq. in. we have detected a decided caustic attack of the iron by solutions as concentrated as 250 grams of sodium hydroxide per liter. The caustic attack consists of the formation of colloidal metallic iron in solution without the formation of hydrogen equivalent, in the ordinary sense, to the iron lost to the solution. This attack is quite uniform over the surface of iron stressed above the yield point, and not extremely rapid. In fact, the reaction with pure water is of comparable speed, one-third to one-half the speed, so the results of the authors are probably in agreement with our own. We do not believe that this caustic attack could possibly be due to the very small amount of silica that is present. However, we believe that the authors recognize this attack in their use of the term "short-time" tests.

The results that indicate that both "chemically pure sodium hydroxide solutions and sodium silicate sodium hydroxide solutions have a much more pronounced effect on this specimen with localized stress than on the concentric-ground specimen with more stress distribution" are extremely interesting and check our results exactly. We find the wires that are stressed with an equal distribution of stress above the yield point and are simultaneously subjected to the sodium hydroxide-sodium silicate attack have no significant decrease in the tensile strength in spite of the presence of silicates. Specimens that have regions of differential stress distribution have their tensile strength rapidly decreased. The sharper the differential of the stress distribution, the more rapid the decrease in the tensile strength.

The attack of pure sodium hydroxide is different from that of sodium hydroxide-sodium silicate mixtures in several particulars. We are engaged in experiments designed to determine the extent of this difference and the theoretical explanation.

We would emphasize: (1) *differential* stress distribution, with the presence of a stress beyond the yield point, (2) contact with concentrated caustic solutions, and (3) presence of silicates in the caustic solutions as essential conditions for the production of one type of intercrystalline failure of iron.

E. G. HILL.—I assume that this embrittlement is caused by hydrogen. Students of the flotation process have an idea of what small amounts of sodium silicate will do in pulps and how they affect the gas absorption on the solids present. This might give a lead as to what is causing the phenomenon being discussed.

F. N. SPELLER,* Pittsburgh, Pa.—To try to explain these results at the present time would be more or less of a guess, for lack of information, but in investigations of this kind we finally seem to get down to problems in surface chemistry and the study of the interfering layer that forms between the solution and the metal. We know little about the structure and composition of such layers, partly because they are often very thin, sometimes of molecular dimensions. However, one or two facts from similar investigations may have a bearing on this problem.

The actual amount of chemical attack is evidently not so important. It is more a question of the concentration of attack on limited areas where the stress may break the film, opening the way to cutting a chemical notch. This causes more stress concentration and may lead to failure by fatigue.

Last year we made a study of corrosion-fatigue in the drilling muds used in the oil fields in rotary drilling. Gel-forming colloids in the mud fluid used in drilling turned out to be the controlling factors. If these were low in amount or absent, we got a short-time failure under a certain stress. When more than a certain amount of these colloids was present the metal was uninjured for a much longer period under the same load, other conditions being the same. Apparently the colloids did not stop corrosion, but it was much more uniformly distributed without forming pits or notches,

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at least within the limits of these fatigue tests. In one case we noticed a multitude of very fine cracks distributed within a stress range of from 23,000 to 30,000 lb., whereas tests made in the water with which the mud was made caused one or two deep cracks at the maximum stress, which naturally resulted in early failure under the latter stress. In some cases we found no failures or a relatively high resistance to corrosion fatigue where there was considerable uniform over-all corrosion, but in other cases fatigue cracks developed where the over-all corrosion was considerably less.

It is just possible that these colloids may be an important factor in controlling chemical action and cracking in boilers. Will the authors tell us how they differentiate between hydrogen embrittlement and corrosion?

W. H. SMITH,* Detroit, Mich.—It would be well to require a complete analysis of steels on which papers affecting such popular items as corrosion or physical failures are presented before this Institute. The Bureau of Mines could furnish the base materials from which such tests are to be made. The importance of selecting such materials may be realized from the report of Williams and Sullivan in *Metals and Alloys* (October, 1934) which states that 60 per cent of the material going into the open hearth is scrap; also, that there are some 13 different metallics and oxides in varying qualities in such scrap. If the Bureau of Mines were to supply the basic materials and give full analysis in relation to impurities especially we would have a more comprehensive understanding of the technique affected.

R. E. SUMMERS,† Corvallis, Ore. (written discussion).—It is inconceivable that we have neglected for so long consideration of the possible effect of silicon, the silicates, and especially of silica, in boilers. All metallurgy shows the great influence of minor impurities on physical properties of the metals. In boiler-water chemistry we have postponed to the limit recognition of SiO_2 as a scale former. Yet silica is composed of the two most abundant elements of the earth. To its colloid-forming tendency SiO_2 owes relation to much discussed but least understood boiler-water reactions. From silicon the oxide inherits a multiform activity akin to that of its neighbor, carbon, in group IV of the periodic table. The boiler engineer is being forced to pioneer in a special field of chemistry in which silicon may prove to be a characteristic element.

Experience leads this reviewer to offer the warning that results obtained with synthetic sodium silicate waters, enlightening as those results may be, are not to be interpreted directly into boiler-operating practice. Water-borne silicates of nature incorporate sodium as an important constituent in perhaps the minority of cases. True, many water treatments in use in boiler plants do raise the sodium contents of waters and the direct agency of embrittlement attack on metal has been thought to be sodium hydroxide.

More weight than that imputed to it by Messrs. Schroeder and Berk might accrue to the finding that embrittling action apparently subsides with high concentrations of SiO_2 in caustic solutions. With the low-sulfate, high-silicate waters of western Oregon no proved cases of embrittlement have yet been brought to light, even where boilers are often operated in direct nonobservance of accredited sulfate-alkalinity ratios.

W. C. SCHROEDER AND A. A. BERK (written discussion).—It is perfectly true, as Mr. Moore says, that the stress relations in the eccentric-grooved specimens are not known and probably cannot be accurately computed. The combined stresses, however, more nearly approximate conditions under which boiler fractures occur

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† Assistant Professor of Mechanical Engineering, Oregon State College.

than would a tensile stress alone. Since the primary object of the study is to compare the action of the various solutions with that of water or air under exactly the same conditions, it is only necessary that the specimen be reproducible. This type of test specimen makes possible a study of the protective effect of various salts under optimum conditions for the production of embrittlement.

It is apparent from the tables that a parallel study is being made with specimens stressed in pure tension. Even with uniform load conditions, however, it has been shown by Möller and Barbers that localized stresses much greater than the calculated average stress⁶ can exist. It is probable that these local stresses are most important in the production of embrittlement in steel.

The satisfactory agreement between the conclusions reached by Mr. Chittum and Mr. Ritchey and those in our paper probably indicates that the experimental study of embrittlement is on a much firmer footing than hitherto it has been. The results in Table 4 are intended to indicate that the sodium hydroxide has no markedly different effect from water as measured by the tension tests on the concentric-ground specimens. Tables 9 and 10 show that the chemically pure sodium hydroxide has quite a different effect from water on the eccentric-grooved specimens. In further tests⁶ it has also been found that the effect of the pure sodium hydroxide on the eccentric-grooved specimen was not due to the small amount of sodium silicate present.

As stated by Dr. Speller, there appears to be no direct relationship between the amount of over-all attack of the metal by the solution and the embrittlement of the metal. Fatigue and stress concentration may be of importance^{7,8}. These factors and the part played by hydrogen in the embrittlement reactions are being investigated at the present time. The effect of colloids in the reactions should also be well worth further consideration.

Mr. Summers has pointed out that the tendency for the higher concentrations of sodium silicate to delay failure of the specimen may be of marked importance. The same result has been checked in further testing⁶, and it has been found that the ratio of sodium silicate to sodium hydroxide may also enter into the reactions. These results point to the necessity for extreme caution in allowing boiler waters which contain relatively high sodium silicate concentrations to attain excessively high sodium hydroxide concentrations at the same time.

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